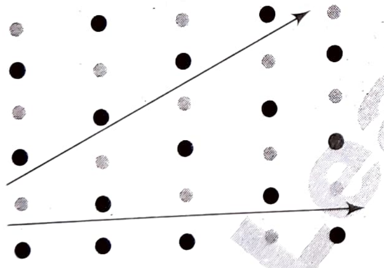
CHAPTER 1

DPP 1.1

Subjective Type

1. Any material can be made amorphous or glassy either by rapidly cooling its melt or freezing its vapours.
   For example, silica (SiO_2) crystallizes as quartz in which SiO_4 tetrahedra are linked in a regular manner but on melting and then rapid cooling, it gives glass in which SiO_4 tetrahedra are randomly joined to each other. Thus, quartz is crystalline SiO_2 whereas silica glass is amorphous SiO_2.
2. On heating, amorphous substances change to crystalline form at some temperature. Some objects from ancient civilization are found to be milky in appearance. This is due to crystallization.
3. When a particular substance exists in more than one crystalline form, the property is called polymorphism, e.g., calcium carbonate exists in two crystalline forms called calcite and aragonite. In case of elements, this property is called 'allotropy'.
4. A solid is said to be crystalline if its various constituent particles (i.e., ions, atoms or molecules) are arranged in a definite geometric pattern in 3D space. Crystalline substances are anisotropic. The anisotropy exhibited by crystalline substances is obviously due to the fact that in making measurements in different directions, different types of particles fall on the way as shown in figure.



5. (i) Uncharged atoms and molecules pack more efficiently in a close-packed structure.
   (ii) A cubic unit cell must have the 6 faces same. The highest symmetry possible for an end-centred unit cells is tetragonal.

Single Correct Answer Type

6. (b) A crystal possesses only one centre of symmetry.

7. (b) TiO_2 has tetragonal system with five planes of symmetry and five axes of symmetry.

8. (b) Cubic lattice is bcc type

No. of X atoms at the corner $= \frac{8}{8} = 1$

No. of Y atoms at the body centre $= \frac{1}{1} = 1$

Thus, ratio of $X : Y = 1 : 1$

Thus, formula is XY.

9. (b) For hexagonal $a = b \neq c$ and $\alpha = \beta = 90^{\circ}$ and $= 120^{\circ}$.

10. (a) $f + c = e + 2$; where f is plane faces, c is interfacial angle and e is straight edges.

11. (c) The smallest 3-D portion of a complete space lattice which when repeated over and again in different directions produces the complete space lattice is called the unit cell or basis or motif.

12. (b) Crystalline solid has regular arrangement of constituent particles observed over a long distance in the crystal lattice. Due to this regular arrangement crystalline solid have sharp melting point.

13. (d) Graphite can't be classified as ionic solid as graphite is not made up of ions. It is made up of carbon atoms covalently bonded to three carbon atoms. So, it is a covalent solid. Since, the formation of covalent bond occurs throughout the crystal therefore, it is a type of network solid. Due to presence of free electron, graphite is also classified as conductor solid.

Multiple Correct Answers Type

14. (a, c)
Amorphous solid has short range order which has a tendency to flow very slowly. Hence, it is also known as pseudo solids or super cooled liquids. Glass panes fixed to windows or doors of old buildings are invariably observed to be thicker at bottom than at the top. These are examples of amorphous solids.

15. (a, b)
The crystalline substances possess sharp melting points, for this reason, crystalline solids have definite heats of fusion. In case of crystalline substance, the properties like electrical conductivity, refractive index etc. have different values in different directions. This type of behaviour is called anisotropy.

16. (c, d)
For hexagonal system $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$
For triclinic system $\alpha \neq \beta \neq \gamma \neq 90^{\circ}$

17. (b, c, d)
Only (a) is wrong because in tetragonal system, $a = b \neq c$. In all other cases $a \neq b \neq c$.

18. (b, d)
(a) Diamond is harder than graphite. Hence, (a) is **incorrect.**
(b) Graphite is a good conductor of electricity as each C-atom is attached to three other C-atoms and 4th electron is free while in diamond, all the four valencies are satisfied, it is insulator. Thus, (b) is **correct.**
(c) Diamond is better thermal conductor than graphite. This is because thermal conduction is due to the transfer of thermal vibrations from atom to atom which is easier in a compact crystal like that of diamond. Hence, (c) is **incorrect.**
(d) In graphite, C–C bond acquires some double bond character. Hence, it is has higher bond order than diamond. Thus, (d) is **correct.**

Matching Column Type

19. (A → 2, 3), (B → 3, 4), (C → 3, 5), (D → 1, 4)
(A) For primitive unit cell, $a = b = c$

Total number of atoms per unit cell = 1/8 × 8 = 1

Here, 1/8 is due to contribution of each atom present at corner.

(B) For body centred cubic unit cell, $a = b = c$

This lattice contains atoms at corner as well as body centre. Contribution due to atoms at corner $= \frac{1}{8} \times 8 = 1$

contribution due to atoms at body centre = 8

(C) For face centred unit cell, $a = b = c$

Total constituent ions per unit cell present at corners

$= \frac{1}{8} \times 8 = 1$

Total constituent ions per unit cell present at face centre

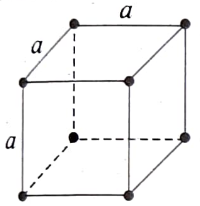
$= \frac{1}{2} \times 6 = 3$

(D) For end centered orthorhombic unit cell, $a \neq b \neq c$

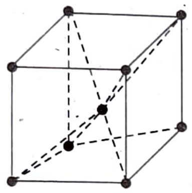
Total contribution of atoms present at corner $= \frac{1}{8} \times 8 = 1$

Total contribution of atoms present at end centre $= \frac{1}{2} \times 2 = 1$

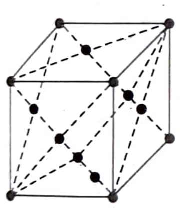
Hence, other than corner it contains total one atom per unit cell.



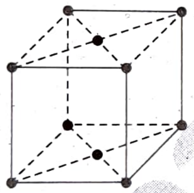
Primitive
(or simple)



Body centred



Face centred



End centred

Integer Type

20. (9) There are four body diagonals. Thus, there are 8 atoms within the body of the unit cell which are not shared by any other unit cell. Contribution by atoms at the corners $= 8 \times \frac{1}{8} = 1$.

Hence, total atoms/unit cell = 8 + 1 = 9.

21. (1) BCC has 2 atoms per unit cell.

1 mole of Na = 23 g = 6.02×10^{23} atoms

$\therefore$ No. of atoms present in 9.2 g of sodium $= \frac{6.02 \times 10^{23}}{23} \times 9.2$

As BCC has 2 atoms per unit cell, number of unit cells present

$= \frac{6.02 \times 10^{23}}{23 \times 2} \times 9.2 = 1.204 \times 10^{23}$

Comprehension Type

22. (b) Ice has hexagonal structure with $a = b \neq c$ & $\alpha = \beta = 90°$, $\gamma = 120°$.

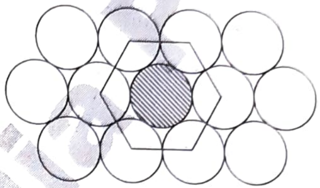
23. (b) Ice has hexagonal structure with $a = b \neq c$ & $\alpha = \beta = 90°$, $\gamma = 120°$.

DPP 1.2

Subjective Type

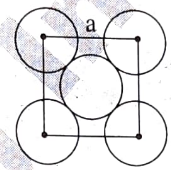
1. (i) $a = 2R$, where a is the length of the side of parallelogram and R is the radius of circle.

(ii) The crystal coordination number (CN) is the number of nearest neighbours around a given atom, ion or molecule in the crystal. Drawing the figure in an elaborated way:



From the figure, each atom is touching six other atoms, so CN = 6

2.



$$4r = \sqrt{2}a$$

$$a = 2\sqrt{2}r$$

put $\eta = \frac{2 \times \pi r^2}{a^2} = \frac{2\pi}{8} = \frac{\pi}{4} = 0.7854$

% efficiency = 78.54%

3. Here, a = 620 pm, d = ?, r = ?

For the face-centred cubic $d = \frac{a}{\sqrt{2}} = \frac{620}{1.414} = 438.5$ pm

$r = \frac{d}{2} = \frac{438.5}{2} = 219.25$ pm.

4. 1 mole of gold = 197 g = 6.02×10^{23} atoms

$\therefore$ No. of atoms present in 1 g of gold $= \frac{6.02 \times 10^{23}}{197}$

As face-centred cubic unit cell contains 4 atoms, therefore, number of unit cells present

$= \frac{6.02 \times 10^{23}}{197 \times 4} = 7.64 \times 10^{20}$.

Single Correct Answer Type

5. (a) The bcc structure has co-ordination no. of eight.

6. (a) Au atoms are at 8 corners of the cube. Thus, number of Au atoms in the unit cell = 8/8 = 1.

Cu atoms are at the face-centres of 6 faces. Therefore, its share in the unit cell = 6/2 = 3.

Thus, formula is $AuCu_3$.

7. (b) It is a fact for crystal structure (bcc) potassium.

8. (a) Packing density in fcc, bcc and sc are 0.74, 0.68 and 0.52 respectively.

9. (a) Radius of Na (if bcc lattice) $= \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}\times 4.29}{4} = 1.8574\,\text{Å}$.

10. (c) The plane is passing through 6 atoms present on two opposite face diagonals.

11. (b) In bcc $r = \frac{\sqrt{3}a}{4}$

Also, edge length of unit cell $= a$

Radius of atom $= r$

$\therefore$ edge length not covered by atom $= a - 2r$

$$\text{or } = a - \frac{\sqrt{3}}{2}\cdot a$$

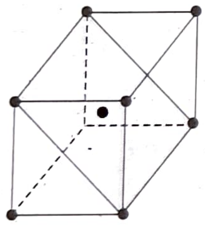
$$= a\left[\frac{2-\sqrt{3}}{2}\right]$$

$\therefore$ Percentage fraction not covered

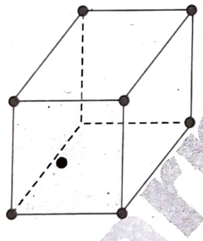
$$= \frac{a\frac{2-\sqrt{3}}{2}}{a}\times 100 = 0.134\times 100 = 13.4\%.$$

Multiple Correct Answers Type

12. (a, d)



Body-centered cubic [Central atom touches other four atoms in the shaded plane]



Face-centered cubic [Central atom touches other four atoms in the shaded plane]

13. (a, b, d)

(a) The body diagonal is $\sqrt{3}$ (5.20Å) = 9.01 Å. The nearest neighbors along that diagonal are half that distance apart, 4.50Å

(b) 5.20Å along the cell edge.

(c) 8 (for example, the body-centre is next to 8 corners.)

(d) 6 (The corner has neighbors along each cell edge: up, down, in, out, left, right.)

14. (c, d)

For simple cubic, $a = 2r$ and for bcc, $a = 4r/\sqrt{3}$.

15. (b, c)

Total number of atoms in a unit cell $= \frac{n_c}{8} + \frac{n_f}{2} + \frac{n_b}{1} + \frac{n_e}{4}$

16. (b, c, d)

Number of effective x atoms = 8 corners $\times \frac{1}{8}$ per corner atom share = 1 atom/unit cell

Number of effective y atoms = 6 faces $\times \frac{1}{2}$ per face atom share = 3 atom/unit cell.

Zeff $(8x + y) = 1 + 3 = 4$

Formula of the compound $= x_1y_3$

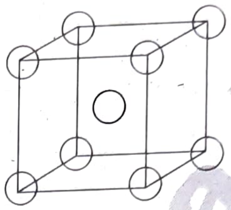
Matching Column Type

17. (a → s), (b → p, q), (c → q, r), (d → r, s)

The results are clear from the figures.

Integer Type

18. (8)



The centre atom of 1 will be at corner of 2. Hence cube 2 divide volume by 8.

$$\therefore \frac{a^3}{8} = \frac{64}{8} = 8\ \text{pm}^3.$$

19. (6) For bcc $r = \frac{\sqrt{3}a}{4}$

Comprehension Type

20. (a) Au atoms/unit cell $= \frac{1}{8}\times 8 = 1$

Cu atoms/unit cell $= \frac{1}{2}\times 6 = 3$

$\therefore$ empirical formula is $AuCu_3$.

21. (a) **Body centred cubic:** $r = \frac{\sqrt{3}a}{4}$;

The unit cell of body centred cubic has 2 atoms on the average.

$$\therefore \text{Volume of atoms } = 2\times\frac{4}{3}\pi r^3$$

$$= 2\times\frac{4}{3}\times\pi\times\left[\frac{\sqrt{3}a}{4}\right]^3 = \frac{\sqrt{3}}{8}\pi a^3$$

Volume of unit cell $= a^3$

$$\therefore \text{Packing factor} = \frac{\sqrt{3}}{8}\frac{\pi a^3}{24} = 0.68$$

Simple cubic: $r = \frac{a}{2}$; The unit cell of sc has one atom.

$$\therefore \text{Volume of atom} = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3 = \frac{4\pi a^3}{24}$$

Volume of unit cell $= a^3$

$$\therefore \text{Packing factor} = \frac{4}{24}\frac{\pi a^3}{a^3} = 0.524$$

12. (a) Total strength of H-bonds = 30.8 − 14.4 = 16.4 kJ/mol. There are 6 nearest neighbours, but each H-bond involves 2 molecules.

Thus, total H-bond = $\frac{6}{2} = 3$

$\therefore$ H-bond energy = $\frac{16.4}{3} = 5.5$ kJ

DPP 1.3

Subjective Type

1. (a) **Hydride:** There are 4 atoms per unit cell, and 8 tetrahedral sites per unit cell, for a 2:1 ratio of tetrahedral sites to atoms. The formula would be TiH_2.

Carbide: There are four octahedral sites per unit cell, and the atomic ratio would be 1:1. The formula would be TiC.

(b) The hydrogen atom is small enough to fit into a tetrahedral hole, but the carbon atom is not.

2. Number of constituent units in packing = $0.5 \times 6.023 \times 10^{23}$

Number of octahedral voids = $0.5 \times 6.023 \times 10^{23}$

Number of tetrahedral voids = $2 \times 0.5 \times 6.023 \times 10^{23}$

Total number of voids = $1.5 \times 6.023 \times 10^{23}$

3. ABAB... Type of packing means hexagonal close packing.

Number of atoms in hcp per unit cell

$= 12 \times \frac{1}{6}$ (corners) + $2 \times \frac{1}{2}$ (face-centred) + 3 (in the body)

$= 6$

Number of octahedral voids = 6

Number of tetrahedral voids = 2 × 6 = 12

4. Packing fraction = volume of atoms per unit cell/volume of unit cell.

$$\therefore \text{Packing fraction of hcp} = \frac{6 \times \frac{4}{3}\pi r^3}{24\sqrt{2}r^3}$$

$$= 0.74$$

% volume occupied = 74%

% volume empty space = 26%.

5. Diamond is a covalent crystal in which each C-atom is sp^3 hybridized. Thus, each C-atom is covalently bonded to four other C-atoms tetrahedrally. These tetrahedral are linked together into a three dimensional giant molecule.

The structure of diamond is similar to that of ZnS. In diamond, we have C-atoms in place of Zn^{2+} and S^{2-} ions. Thus, diamond has face-centred cubic structure in which C-atoms are present at the corners as well as face-centres and alternate tetrahedral voids.

Contribution of C-atoms at the corners = $8 \times \frac{1}{8} = 1$

Contribution of C-atoms at face-centres = $6 \times \frac{1}{2} = 3$

As four C-atoms are present on the body diagonals, i.e., in the alternate voids, their contribution = 4

$\therefore$ Total no. of C-atoms in the unit cell = 1 + 3 + 4 = 8

Single Correct Answer Type

6. (b) It is a fact. Four out of 8 tetrahedral voids are occupied by carbon.

7. (a)
$$AC = \sqrt{AB^2 + BC^2}$$
$$= \sqrt{(2r)^2 + (2r)^2}$$
$$r + r + 2R = 2\sqrt{2}\,r$$
$$\therefore \quad 2R = 2(\sqrt{2}r - r)$$
$$R = (\sqrt{2} - 1)r, \frac{R}{r} = 0.41$$
$$\therefore \quad \frac{r}{R} = 2.41$$

8. (a) Suppose the number of selenide ions in the packing = n

$\therefore$ No. of tetrahedral holes = $2n$

As all of the tetrahedral voids are occupied, therefore, number of lithium ion present = $2n$

Ratio = $2n : n = 2 : 1$

$\therefore$ Formula of lithium selenide is Li_2Se.

9. (c) In hcp, there is 6 atoms per unit cell.

$\therefore$ Number of octahedral voids = 6

$\therefore$ Number of tetrahedral voids = 2 × 6 = 12

$\therefore$ Total number of voids per atom = $\frac{18}{6} = 3$

$\because$ In 1 mole compound the total no. of voids = $3 \times 6.023 \times 10^{23}$

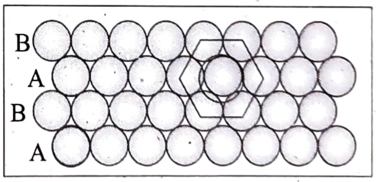
$\therefore$ In 0.5 mole compound the total no. of voids $= 3 \times 0.5 \times 6.023 \times 10^{23} = 9.034 \times 10^{23}$.

10. (b) Packing efficiency is the percentage of total filled space by particles and it can be calculated as packing efficiency

$$= \frac{\text{Volume occupied by four spheres in the unit cell}}{\text{Total volume of unit cell}}$$

Since, packing efficiency for hcp or ccp is calculated to be 74% which is maximum among all type of crystals.

11. (d) Hexagonal close packing can be arranging by two layers A and B one over another which can be diagrammatically represented as



Here, we can see easily that 1st layer and 4th layer are not exactly aligned.

Thus, statement (d) is not correct while other statements (a), (b) and (c) are true.

12. (d) ABABAB … Packing also has void fraction of 0.26.

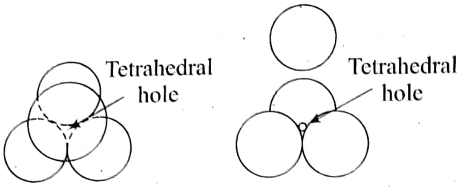
Multiple Correct Answers Type

13. (a, d)

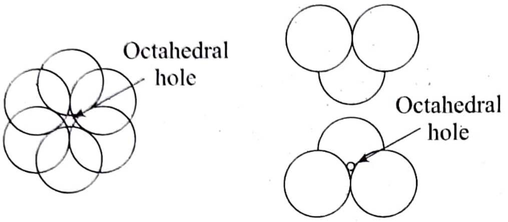
In hcp and fcc arrangement octahedral voids are formed. In fcc, the octahedral voids are observed at edge and centre of cube while in bcc and simple cubic, no octahedral voids are observed.

14. (c, d)

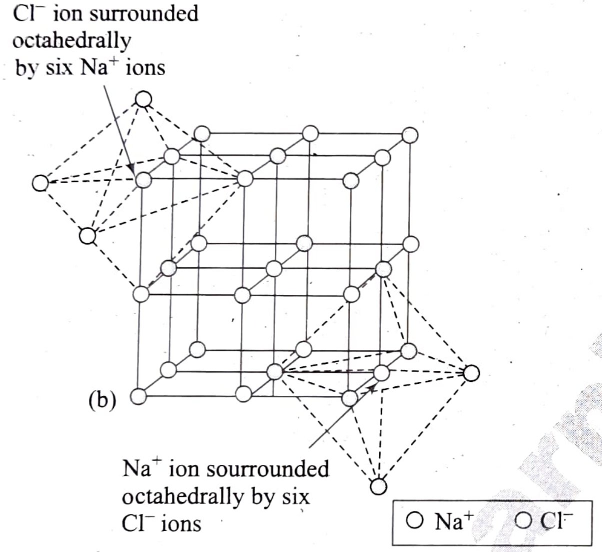
Tetrahedral voids are formed when the triangular void in the second layer lie exactly above the triangular voids in the first layer and the triangular shape of these voids oppositely overlap.


Tetrahedral hole
Tetrahedral hole

Octahedral voids are formed when triangular void of second layer does not exactly overlap with similar void in first layer.


Octahedral hole
Octahedral hole

15. (a, b)


Cl$^-$ ion surrounded octahedrally by six Na$^+$ ions
(b)
Na$^+$ ion sourrounded octahedrally by six Cl$^-$ ions
○ Na$^+$ ○ Cl$^-$

NaCl possesses fcc structure. It is clear from the figure that octahedral voids are located at edge-centre and body-centre.

16. (c, d)

Both have 74% occupied space.

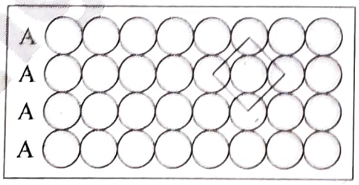
17. (b, c)

Fact

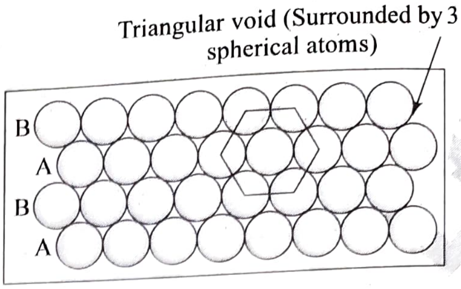
Matching Column Type

18. (a → 3), (b → 1), (c → 4), (d → 2)

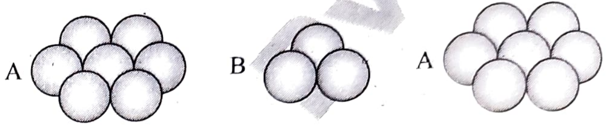
(a) Square close packing in two dimensions. Each sphere have coordination number 4, as shown below.



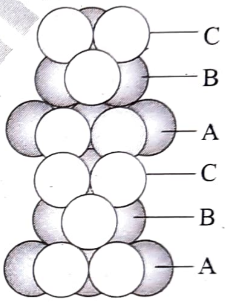
(b) Hexagonal close packing in two dimensions. Each sphere have coordination number 6 as shown below and creates a triangular void.


Triangular void (Surrounded by 3 spherical atoms)
B
A
B
A

(c) Hexagonal close packing in 3 dimensions is a repeated pattern of sphere in alternate layers also known as ABAB pattern.



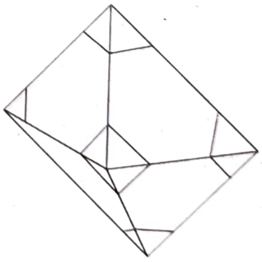
Cubic close packing in a 3 dimensions is a repeating pattern of sphere in every fourth layer.



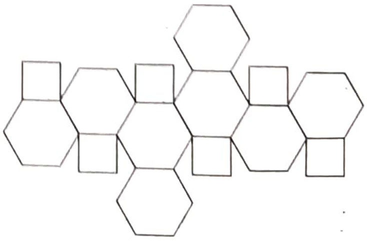
Truncated octahedron unfolded in two-dimension.

Integer Type

19. (6) The truncated octahedron is the 14-faced Archimedean solid with 14 total faces: 6 squares and 8 regular hexagons.
The truncated octahedron is formed by removing the six right square pyramids one from each point of a regular octahedron as:

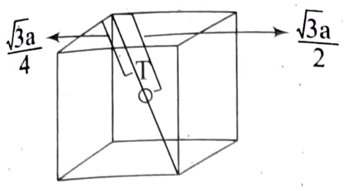


Truncated octahedron



(6) Distance between O void and T void

$$= \frac{\sqrt{3}a}{2} - \frac{\sqrt{3}a}{4} = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3}\times 7}{2} = 6.062 \text{ pm}$$

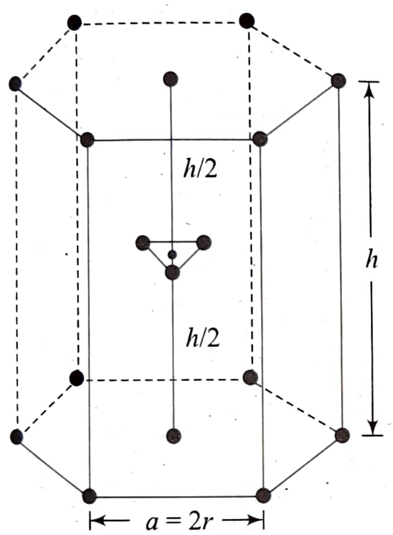


Comprehension Type

(b)

(a)

(a) In this arrangement three atoms are arranged in the body centre position in such a way, so that it forms equilateral triangle and twelve atoms are placed at 12 corners and two atoms at two face centres.



(i) **No. of atoms per unit cell**

$$= \frac{1}{6}\times 12 + \frac{1}{2}\times 2 + 3 = 6$$

(ii) $V = h \times \text{area} = 6\sqrt{3}r^2 \times 4r \times \sqrt{\frac{2}{3}} = 24\sqrt{2}r^2$

(iii) **Packing fraction:** Each corner atom would be common to 6 other unit cell. If r is the radius of each sphere, then

$$\text{Packing fraction} = \frac{6 \times \frac{4}{3}\pi r^2}{v}$$

where, v = volume of hexagon = Area of base (A) × height (h)

$$\therefore \text{Packing fraction} = \frac{6\times\frac{4}{3}\pi r^2}{6\times\sqrt{3}r^2\times 4r\times\sqrt{\frac{2}{3}}} = \frac{\pi}{3\times\sqrt{2}}$$

$$= 0.74 \text{ or } 74\%$$

The remaining 26% space which is vacant, constitutes **interstitial voids or interstices sites or interstices.**

DPP 1.4

Subjective Type

1. This is due to their smaller radius ratio. Any attempt to pack 8 anions around the relatively small cation (Li^+, Na^+, K^+, Rb^+) will produce a state in which negative ions will touch each other, sooner they approach a positive ion. This causes unstability to the lattice.

2. Increase of pressure increases the coordination number whereas increase of temperature decreases the coordination number. For example:

$$\underset{(6:6)}{\text{NaCl structure}} \underset{760\text{ K}}{\overset{\text{Pressure}}{\rightleftharpoons}} \underset{(8:8)}{\text{CsCl structure}}$$

On applying high pressure, NaCl structure having 6:6 coordination changes to CsCl structure having 8:8 coordination. Similarly, CsCl having 8:8 coordination on heating to 760 K changes to NaCl structure having 6:6 coordination.

3. (i) Maximum radius ratio in ionic crystals lies in the range 0.732 – 1 which corresponds to a coordination number of 8. Hence, coordination number greater than 8 is not possible in ionic crystals.

(ii) CsCl is more stable than NaCl. This is because higher the coordination number, greater are the forces of attraction between the cations and the anions in the close-packed arrangement. As CsCl has co-ordination number of 8:8 while NaCl has a coordination number of 6:6, therefore, CsCl is more stable.

4. In a unit cell, there are one Cs^+ and $\frac{1}{8}\times 8 = 1\,Cl^-$, i.e., one CsCl molecule.

$$\because \quad \text{Density} = \frac{n\times\text{molar mass}}{V\times\text{Av. no.}} = \frac{n\times\text{molar mass}}{a^3\times\text{Av. no.}}$$

$$\therefore \quad 3.97 = \frac{1\times 168.36}{a^3\times 6.023\times 10^{23}}$$

$$a = 4.13\times 10^{-8} \text{ cm}$$

$$\therefore \quad a = 4.13 \text{ Å}$$

For a cube of side length 4.13 Å, diagonal = $\sqrt{3}\times 4.13 = 7.15$ Å

As it is a bcc with Cs^+ at centre (radius r^+) and Cl^- at corners (radius r^-), so

$2r^+ + 2r^- = 7.15$ or $r^+ + r^- = 3.57$ Å

i.e., Distance between neighbouring Cs^+ and Cl^- = 3.57 Å

Now assume two Cl^- ions touch each other, so

Length of unit cell = $2r^-$ = 4.13 Å $\therefore r^- = 2.06$ Å

$\therefore \quad r^+ = 3.57 - 2.06 = 1.51$

$\therefore \quad r^+/r^- = 1.51/2.06 = 0.73$

Single Correct Answer Type

5. (d) All these are characteristics of ferrites.
6. (b) In bcc structure co-ordination no. is eight.
7. (c) In antifluorite crystal (Na_2O) the anions are arranged in cubic close packing while the cations occupy all the tetrahedral voids.
8. (c) This leads to stronger coulombic forces of attractions in NaF.
9. (d) NaCl possess rock-salt type structure with formula AB. ZnS possess Sphalerite type structure with formula AB.

10. (a) Effective number of remaining $Cl^- = 4 - \left[2 \times \frac{1}{8} + \frac{1}{2}\right] = \frac{13}{4}$

Effective number of $Na^+ = 4$

$$\text{Packing fraction} = \frac{\text{Occypied volume}}{\text{Total volume}}$$

$$= \frac{\frac{13}{4} \times \frac{4}{3}\pi r_-^3 + 4 \times \frac{4}{3}\pi r_+^3}{8(r_+ + r_-)^3} = \frac{\frac{13}{3}\pi r_-^3 + \frac{16}{3}\pi r_+^3}{8(r_+ + r_-)^3}$$

11. (b) $\frac{r_{Na^+}}{r_{Cl^-}} = \frac{95}{181} = 0.524$, i.e., in between 0.414 to 0.732 and thus, co-ordination no. = 6

12. (a) $d = \frac{n \times \text{atomic mass}}{a^3 \times \text{Av. no.}}$

$$\Rightarrow \quad 2.165 = \frac{n \times 58.5}{(562 \times 10^{-10})^3 \times 6 \times 10^{23}}$$

∴ $n = 4$ rank of unit cell

∴ AB has fcc structure.

$$\therefore \quad d_{A^+-B^-} = \frac{a}{2}.$$

13. (a) $\frac{d_\gamma}{d_\beta} = \frac{d_{\text{fcc}}}{d_{\text{bcc}}} = \frac{n_\gamma \times (a_\beta)^3}{n_\beta \times (a_\gamma)^3}$

$$= \frac{4}{2} \times \left(\frac{290}{386}\right)^3 = 0.9788.$$

14. (b) Let x Cu^{2+} and $(1.8 - x)$ Cu^+ ions are present in the compound $Cu_{1.8}S$. Compound is electrically neutral.

$\therefore \quad + 2x + (1.8 - x) - 2 = x = 0.2$

$$\% \ Cu^{2+} = \frac{0.2}{1.8} \times 100 = 11.11$$

15. (b) Rock salt – simple cubic

$$r_A^+ + r_B^- = \frac{a}{2}$$

$$75 + r_B^- = \frac{400}{2}$$

$$r_B^- = 200 - 75 = 125 \text{ pm}$$

Multiple Correct Answers Type

16. (a, b, c)
NaCl has 74% of occupied space.

17. (c, d)
In both ZnS and Na_2O, the cations are situated at octahedral voids.

18. (a, b, d)
Cl^- ions are present at each corner of the cube.

19. (a, b, c)
Na_2O has antifluorite structure in which O^{2-} ions are present in ccp while Na^+ ions occupy all the tetrahedral voids which are located at body diagonals.

20. (a, b, c, d)

(a) NaCl have fcc structure so nearest neighbour distance = $a/2$

(b) CaF_2 has ccp arrangement in which Ca^{2+} ions form fcc with each Ca^{2+} ion surrounded by $8F^-$ ion occupy all tetrahedral voids.

(c) In Na_2O, negative ions form ccp arrangement so that each positive ion is surrounded by 4 negative ions and each negative ion by 8 positive ions. The cations occupy half of the tetrahedral voids. So nearest neighbor distance in CaF_2 and $Na_2O = a\sqrt{3}/4$.

(d) CaCl has bcc arrangement so nearest neighbor distance = $a\sqrt{3}/2$.

Matching Column Type

21. (a → q), (b → s), (c → r), (d → p)

(a) It is an example of Zinc blende type structure

(b) This type of structure is shown by CsCl types

(c) Antifluorite type structure has such type of arrangement

(d) Rock salt type of structure has coordination number 6:6 and cations have fcc arrangement and anions occupy all octahedral voids.

Integer Type

22. (5) AB has rock salt (A : B = 1 : 1) structure, i.e., fcc structure (n = 4) and formula mass of BB is 6.023 y g having closest distance A – B $y^{1/3}$ nm. Therefore edge length of unit cell

$$a = 2(A^+ + B^-) = 2 \times y^{1/3} \times 10^{-9} \text{ m}$$

$$\therefore \quad \text{Density of AB} = \frac{n \times \text{molar mass}}{\text{Av. no.} \times V}$$

$$= \frac{n \times \text{molar mass}}{6.023 \times 10^{23} \times a^3}$$

$$= \frac{4 \times 6.023 \times y \times 10^{-3}}{6.023 \times 10^{23} \times (2y^{1/3} \times 10^{-9})^3}$$

(molar mass in kg mol^{-1})

$$= 5.0 \text{ kg m}^{-3}.$$

23. (7) In a cell, there are one Cs^+ and $\frac{1}{8} \times 8 = 1 \, Cl^{-1}$, i.e., one CsCl molecule

$$\therefore \quad \text{Density} = \frac{n \times \text{molar mass}}{V \times \text{Av. no.}} = \frac{n \times \text{molar mass}}{a^3 \times \text{Av. no.}}$$

$$\therefore \quad 3.97 = \frac{1 \times 168.36}{a^3 \times 6.023 \times 10^{23}}$$

$a = 4.13 \times 10^{-8}$ cm

∴ $a = 4.13$ Å

For a cube of side length 4.13 Å,

diagonal $= \sqrt{3} \times 4.13 = 7.15$ Å

Comprehension Type

24. (c) Spinels are compounds with two different cations A^{2+} and B^{3+} and oxides (O^{2-}) as the anion, with the general formula $A^{2+}B_2^{3+}O_4^{2-}$.

25. (a) Divalent cation (Zn^{2+}) occupy 1/88th of the tetrahedral voids.

26. (a) There are four O^{2-} ions in the unit cell; let these ions are replaced by n, $X^{-8/3}$ ions.

Charge of O^{2-} ions = Charge of $X^{-8/3}$ ions

$4(-2) = n(-8/3)$

$n = 3$ (i.e., there will be one ionic vacancy)

Thus, there will be one ionic vacancy per unit cell.

DPP 1.5

Subjective Type

1. (a) B is a group-13 element and Si is a group-14 element, there will be a positive hole. Hence, it is p-type.

(b) When a cation of higher valency is added, then two or more cations of lower valency are replaced to maintain electrical neutrality, the some cation vacancies are produce. For example, when $CdCl_2$ is added to AgCl, cation vacancies are created because two Ag^+ ions are replaced by a Cd^{+2} ion.

2. Silicon normally forms 4 covalent bonds with neighboring atoms. When it is doped with P, the Si atoms at some lattice sites are substituted by atoms of P. Now as these atoms have 5 electrons in the valence shell, after forming normal 4 covalent bonds with the neighbouring Si atoms, the fifth extra electron is free and delocalized. These delocalized electrons increase the conductivity of Si. As the increase in conductivity is due to negatively charged electrons, the Si crystal doped with electron rich impurities are called and type semi-conductor.

3. (i) Frenkel defects are found in silver halides (AgCl, AgBr and AgI) due to small size of Ag^+ ion. It is also shown by ZnS due to small size of Zn^{2+} ion. They are not found in alkali metal halides as the alkali metal ions cannot fit into the interstitial sites.

(ii) As the number of ions decreases as a result of this defect, the mass decreases whereas the volume remains the same. Hence, like vacancy defect, the density of the solid decreases. It is observed that in NaCl crystal at room temperature, there are about 10^{22} ions and 10^6 Schottky pairs per cm^3. This means that there is one Schottky pair defect per 10^{16} ions. Thus, there are large number of holes present in the crystal. This result in the decrease in the density.

4. 1 mole of NaCl contains 1 mole of Na^+ ions, i.e., 6.023×10^{23} Na^+ ions.

NaCl has fcc arrangement of Cl^- ions and Na^+ ions are present at the edge centres and body centre. As there are 12 edge centres and each edge centre is shared by 4 unit cells, their concentration per unit cell $= \frac{1}{4} \times 12 = 3$.

Concentration of Na^+ ion at the body centre = 1

Thus, for every 4 Na^+ ions, the ions present at the edge centres = 3. This means that Na^+ ions which have been replaced = $\frac{3}{4} \times 6.023 \times 10^{23} = 4.517 \times 10^{23}$

1 Al^{3+} ion will replace 3 Na^+ ions to maintain electrical neutrality. One vacancy will be occupied by Al^{3+} ion and the remaining 2 will be vacant.

This means that $\frac{1}{3}$rd of these positions will be occupied by Al^{3+} ions $\frac{2}{3}$rd will remain vacant.

Hence, no. of vacancies in 1 mole of NaCl = $\frac{2}{3} \times 4.517 \times 10^{23}$

$= 3.01 \times 10^{23}$.

Single Correct Answer Type

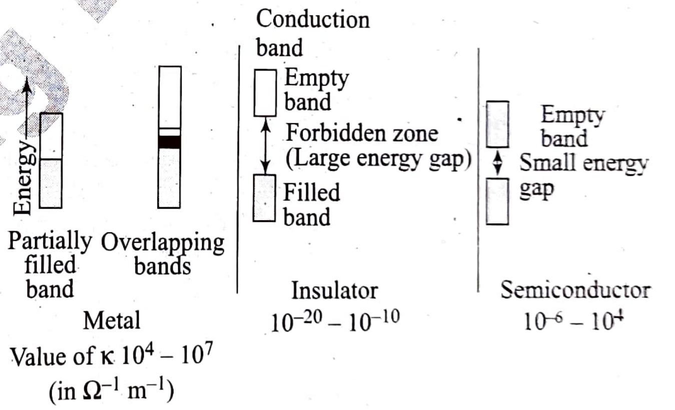
5. (b) The ions leave its correct lattice site and occupies an interstitial site.

6. (d) Schottky defects arise when one positive ion and one negative ion are missing from their respective positions leaving behind a pair of holes. These are more common in ionic compounds with high coordination number and having almost similar size of cations and anions.

7. (d) The transition of metal to insulation occurs at a certain temperature due to imperfection.

8. (b) Pentavalent impurities in Ge gives n-type semiconductors.

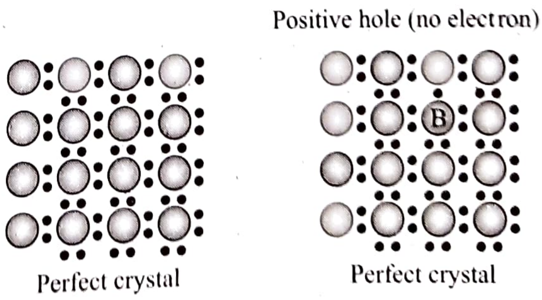
9. (a) Conductivity of metal, insulator and semiconductors can be represented in the term of κ (Kappa) which depends upon energy gap between valence band and conduction band.



Hence, correct order is

$\kappa_{metals} >> \kappa_{insulators} < \kappa_{semiconductors}$

10. (b) When group-13 elements are doped in group-14 element, it creates a hole in a molecule but the molecule as a whole remain neutral. Thus, p-type semiconductor is neutral in nature.



11. (b) Let x and y be the Fe^{2+} and Fe^{3+} ions respectively, we will have

$x + y = 0.93$

Also, $2x + 3y = 2$

Solving for y, we get $y = 0.14$

Hence, percentage of Fe^{3+} ions = $(0.14/0.93) \times 100 = 15$.

Multiple Correct Answers Type

12. (b, c)
Frenkel defect is present in those compounds which have large difference in the size of cations and anions like ZnS. In Schottky defect has the number of ion decreases, density of the solid also decreases.

13. (a, b)
In Frenkel defect as no ions are missing from the crystal as a whole, therefore density of the solid remains unchanged and as similar charges come closer, this results in the increase of dielectric constant of the crystals.

14. (a, b, d)
Excess of Li in LiCl makes it pink.

15. (a, d)
When KCl crystals are heated it leads to the deposition of potassium ion on surface of KCl. The Cl^- ions diffuse to the surface of crystal and lose electron by potassium atom to form K^+ ion released electron occupies anionic site which is known as F-centre and impart colour to the crystal.

16. (b, d)
Vacancy and Schottky defects which lead to decrease in the density. Both are the types of a stoichiometric defect. In case of Frenkel defect and interstitial defect, there is no change in density of substance.

Matching Column Type

17. (a → p, r), (b → q), (c → p, q), (d → p, s)
Schottky defect is exhibited by NaCl, AgBr and KCl and ZnS and AgBr exhibits Frenkel defect.
Due to metal excess defect in NaCl and KCl, NaCl develops yellow colour and KCl develops blue colour.

Integer Type

18. (2) Z_{eff} of Ca = 4 atoms/unit cell
Since there are 0.1% Schottky defect,

$$\text{So } Z_{eff} = \left(4 - \frac{0.1}{100} \times 4\right) = 3.996$$

$$\therefore\ \rho = \frac{Z_{eff} \times Aw}{N_A \times a^3} \qquad (\because 1\ nm = 10^{-9}\ m = 10^{-7}\ cm)$$

$$= \frac{(3.996) \times 40\ g}{(6 \times 10^{23}\ mol^{-1})\ (0.500 \times 10^{-7}\ cm)^3} = 2.13 \approx 2\ g\ cm^{-3}.$$

19. (2)
$$\rho_{theoretical} = \frac{N \times mol.wt}{a^3 \times N_a} = \frac{4 \times 40}{(0.50 \times 10^{-7})^3 cm^3 \times 6 \times 10^{23}}$$

$$= \frac{160}{0.75 \times 10^{-21+23}} = 2.133\ g/cm^3$$

$$\%\ missing = \frac{\rho_{theo} - \rho_{exp}}{\rho_{exp}} \times 100$$

$$0.25 = \frac{2.13 - \rho_{exp}}{2.13} \times 100$$

$$0.00532 = 2.13 - \rho_{exp}$$
$$\rho_{exp} = 2.124\ g/cm^3$$

Comprehension Type

20. (b) When Si is doped with group 15 element, due to presence of extra negatively charged electrons, the Si crystals doped with e^- rich impurities are called *n*-type semiconductors.

21. (a) When Si is doped with e^- deficit impurity an e^- hole is generated and thus, give rise to a *p*-type semiconductor.

22. (c) Doping of NaCl with 10^{-3} mol % $SrCl_2$ means that 100 moles of NaCl are doped with 10^{-3} mol of $SrCl_2$.

$$\therefore\quad 1 \text{ mole of NaCl is doped with } SrCl_2 = \frac{10^{-3}}{100} \text{mole}$$
$$= 10^{-5} \text{ mole}$$

As each Sr^{2+} ion introduces one cation vacancy, therefore concentration of cation vacancies

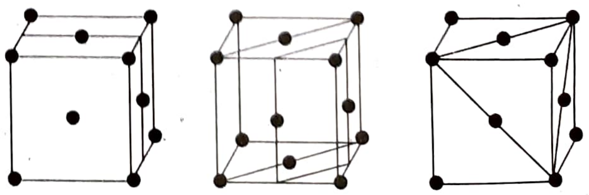
$$= 10^{-5}\ mol/mol \text{ of NaCl}$$
$$= 10^{-5} \times 6.02 \times 10^{23}\ mol^{-1}$$
$$= 6.02 \times 10^{18}\ mol^{-1}$$

23. (b) Flow of +ve hole to the –ve end indicates that it is a *p*-type semiconductor.
Flow of e^-s indicates that it is a *n*-type semiconductor.

DPP 1.6

Subjective Type

1. Ferrimagnetic Fe_3O_4 on heating to 850 K becomes paramagnetic. This is due to greater alignment of domains (spins) in one direction on heating.
2. (a) Levitation occurs when objects float in air due to the mutual repulsion between permanent magnet and a super conductor.
   (b) H. Kamerlingh-Onnes found that down to 4.15 K, the resistance of mercury decreased with decrease in temperature as is the case with most metals. However, fell sharply close to zero. Thus, at or below the critical temperature, mercury became a superconductor.
3. Using Bragg's law, $n\lambda = 2d \sin\theta$, and assuming that the diffractions are of first order ($n = 1$), the distance are calculated to be 0.204 nm, 0.176 nm and 0.124 nm. The distance 0.176 nm is seen to be half the unit cell length, corresponding to the perpendicular distance between layers of atoms in one face of the unit cell and the center. The distance 0.204 nm turns out to be 1 $\sqrt{3}$ times the unit cell length, corresponding to the perpendicular distance between a corner of the unit cell and the plane of the three adjacent corners. The distance 0.124 nm corresponds to $\sqrt{2}/4$ times the unit cell dimension—one-fourth of the distance from one edge of the cell to the opposite edge. The plane intersects the face-centered atoms of two sides. The plane including the edge atoms is equivalent to the plane across the center of the unit cell.



4. CrO_2 is used to make magnetic tapes used for audio recording and its ferromagnetism. Such substances remain permanently magnetised, only they have been magnetised.

Single Correct Answer Type

5. (d) At high temperature randomisation of spins changes.

6. (d) All these are characteristic facts.

7. (c) Ferrimagnetism involves magnetic dipoles oriented in parallel and antiparallel direction in unequal number to give some net dipole moment.

8. (c) $2d \sin\theta = n\lambda$ (Bragg's eqn)

For $n = 1$

$$2d \sin\theta = \lambda$$

(i) If $\theta = 30° \Rightarrow 2d \sin 30° = \lambda$

$\therefore \quad d = \lambda$

(ii) If $\theta = 90° \Rightarrow 2d \sin 90° = \lambda$

$\therefore \quad d = \lambda/2$

9. (d) Substances which are expected to be paramagnetic or ferromagnetic on the basis of unpaired electron but actually they possess zero net magnetic moment are called antiferromagnetic.

10. (c) $n\lambda = 2d \sin\theta$

$$d = \frac{\lambda}{2\sin\theta} \quad \text{...(i) (for first order diffraction)}$$

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{...(ii)}$$

Comparing equations (i) and (ii)

$$\frac{\lambda}{2\sin\theta} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$\sin\theta = \frac{\lambda}{2a}(h^2 + k^2 + l^2)^{1/2}$$

11. (d) All are conductors however they show insulation at a certain temperature.

Multiple Correct Answers Type

12. (a, b)

Chromium has 6 unpaired electrons. Therefore, Cr is paramagnetic not diamagnetic and large number of unpaired electrons are present in ferromagnetic substances.

13. (a, b, c)

Gallium acts as a superconductor at 1.1 K.

14. (c, d)

In the case of antiferromagnetic substances, the magnetic moment becomes zero because the domains are oppositely oriented with respect to each other without the application of magnetic field which cancel out each other.

15. (a, d)

Ferrimagnetic substances lose ferrimagnetism on heating and become paramagnetic. In ferromagnetic substance, domains are aligned in parallel and antiparallel direction in unequal numbers. In ferromagnetic substances, all the domains get oriented in the direction of magnetic field and remain as such even after removing magnetic field.

Hence, (a) and (d) are correct choices.

16. (c)

58.4 pm

$2d \sin\theta = n\lambda \ (n = 1)$

$= 2 \times 0.200 \times 10^{-9} \times 0.1461 = \lambda$

$\lambda = 0.05844 \times 10^3 \text{ pm} = 58.4 \text{ pm}$

Matching Column Type

17. (a → q), (b → s), (c → p), (d → r)

In some of the piezoelectric crystals, the dipoles are permanently polarized even in the absence of the electric field. However, on applying electric field, the direction of polarization changes. This phenomenon is called ferroelectricity.

Some piezoelectric crystals when heated produce a small electric current. The electricity thus produced is called pyroelectricity.

When mechanical stress is applied on such crystals, electricity is produced due to displacement of ions. The electricity thus produced is called piezoelectricity.

Integer Type

18. (2) Applying Bragg's equation,

$n\lambda = 2d \sin\theta$

Given, $n = 1$, $\lambda = 1.54$ Å, $\theta = 22.5°$

Using relation $n\lambda = 2d \sin\theta$

$$d = \frac{1.54}{2\sin 22.5°} = \frac{1.54}{2 \times 0.383} = 2.01 \text{ Å}$$

19. (4) Bragg's eqn. is $2d \sin\theta = n\lambda$ and $d = 4\lambda$, $\theta = 30°$

$\therefore \quad 2(4\lambda) \sin 30° = n\lambda$

$\Rightarrow \quad 2 \times 4\lambda \times \frac{1}{2} = n\lambda$

$\Rightarrow \quad n = 4.$

Comprehension Type

20. (c) As they do not allow the magnetic field to pass through it.

21. (a) Levitation occurs when objects float in air. This can be achieved by mutual repulsion between permanent magnet and a super conductor.

22. (b) The molecules with general formula ABO_3 or ABC_3 possess pervoskite structure.

CHAPTER 2

DPP 2.1

Subjective Type

1. $M_{eq.}$ of $H_2SO_4 = M_{eq.}$ of NaOH

$N \times 5 = 84.6 \times 2$

$\therefore \quad N = \dfrac{84.6 \times 2}{5} = 33.84$ eq. litre^{-1}

$\therefore$ Mass of H_2SO_4 in 1 litre $= 33.84 \times 49$

$\therefore$ Density or mass of H_2SO_4 in 1 mL $= \dfrac{33.84 \times 49}{1000} = 1.658$ g/mL

$\therefore$ Purity $= \dfrac{1.658}{1.8} \times 100 = 92.12\%$

2. Aquatic species are more comfortable in cold water due to the presence of more oxygen. Solubility of oxygen in water increases with decrease in temperature as solubility of a gas in given liquid decreases with increase in temperature.

3. Dissolution of sugar in water will be most rapid when powdered sugar is dissolved in hot water because powder form can easily insert in vacancies of liquid particles. Further dissolution of sugar in water is an endothermic process. Hence, high temperature will favour the dissolution of sugar in water.

4. 109% oleum means it has 9 g H_2O which reacts with free SO_3 to give H_2SO_4.

According to stoichiometry, $SO_2 + H_2O \rightarrow H_2SO_4$

Mass of SO_3 which will react with 9 g $H_2O = \dfrac{80 \times 9}{18} = 40$ g

Let 100 g sample of 109% labelled oleum contain 40 g SO_3 and 60 g H_2SO_4.

$\therefore \quad$ Mole of $H_2SO_4 = \dfrac{60}{98} = 0.6122 = x$

Moles of $SO_3 = \dfrac{40}{80} = 0.5 = y$

$x + y = 1.1122$

$x - y = 0.1122$

$\therefore \quad \dfrac{x+y}{x-y} = \dfrac{1.1122}{0.1122} = 9.91.$

5. ppm of As in drinking water = 15

Thus, 15 g As is present in 10^6 g water

$\therefore$ percentage by mass of As $= \dfrac{15 \times 100}{10^6} = 1.5 \times 10^{-3}$

Molality of As $= \dfrac{15}{75 \times \dfrac{10^6}{10^3}} = 2 \times 10^{-4}$ m

(mole of As $= \dfrac{15}{75}$; $V_{water} = W_{water} = \dfrac{10^6}{10^3}$ kg $= 10^3$ kg).

6. (i) According to Henry's law,

$$\frac{a}{p} = K$$

$\therefore a = 3.1 \times 10^{-2} \times 4 = 0.124$ mol/litre.

(ii) $x_{N_2} = \dfrac{P_{N_2}}{K_H} = \dfrac{0.987}{76480} = 1.29 \times 10^{-5}$

If n represents number of mole of N_2 in 1 litre H_2O or $\left(\dfrac{1000}{18} \text{ mole}\right)$ 55.6 mole H_2O, then

$$x_{N_2} = \frac{n}{n + 55.6} = \frac{n}{55.6} = 1.29 \times 10^{-5}$$

Thus, $n = 1.29 \times 10^{-5} \times 55.6$ mol

$= 7.18 \times 10^{-4}$ mol

$= 0.718$ milli mol.

Single Correct Answer Type

7. (a) According to Henry's law partial pressure of gas in the solution is proportional to the mole fraction of gas in the solution.

$$p = K_H x$$

where, K_H = Henry's constant

Hence, (a) mole fraction is the correct choice.

8. (b) Amount of HCl in 2.0 L of 3.0 M solution

$= (2.0 \text{ L})(3.0 \text{ mol L}^{-1}) = 6.0$ mol

Mass of H_2SO_4 in this solution

$= (6.0 \text{ mol})(98 \text{ g mol}^{-1}) = 588$ g

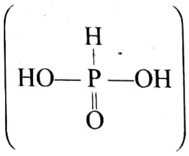
Mass of 96% H_2SO_4 solution containing 588 g of H_2SO_4

$= \dfrac{588 \times 100 \text{ g}}{96} = 612.5$ g

Volume of 96% H_2SO_4 solution weighing 612.5g

$= \dfrac{612.5 \text{ g}}{1.83 \text{ g mL}^{-1}} = 334.7$ mL

9. (d) H_3PO_3



$\left(HO - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}} - OH \right)$ is dibasic acid

$N = n \times M$

$N = 2 \times 0.3 = 0.6$

10. (c) $0.2 = \dfrac{(m/46 \text{ g mol}^{-1})}{(m/46 \text{ g mol}^{-1}) + (1000 \text{ g}/18 \text{ g mol}^{-1})}$

$= \dfrac{m}{46 \text{ g}} = \dfrac{0.2 \times 1000}{18} \times \dfrac{1}{0.8} = 13.89$

$\Rightarrow \quad m = 13.89 \times 46 \text{ g} = 638.89$ g

11. (b)

Gas	Temperature	K_H (K bar)
He	293	144.97
N_2	293	76.48
O_2	293	34.86

Higher the value of Henry's Law constant, the lower is the solubility of the gas in the liquid.

12. (b) $m = kP$

$\ln m = k \ln P + \ln k$

$\log m = \log P + \log K$

Comparing with $y = mx + c$ we get graph given in option (b).

13. (b) From $M = \dfrac{x \times d \times 10}{m_B}$

where d = density of solution containing $x\%$ solute by mass

M = molarity, m_B = molar mass of solute.

14. (c) Milli mole of solution I → 750 × 0.5 = 375

Milli mole of solution II → 250 × 2 = 500

Total milli mole in mixture = 375 + 500 = 875

Total volume = 1000 mL

$\therefore$ Molarity $= \dfrac{875}{1000} = 0.875$ M.

Multiple Correct Answers Type

15. **(a, b, d)**

Melting point of a solute does not affect its vapour pressure.

16. **(c, d)**

Upon adding H_2O to the solution of ionic compound ionization increases and concentration decreases as dilution increases.

17. **(a, d).**

Depending on the vapour pressures of the pure components 1 and 2, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component 1.

18. **(b, c)**

$$M_{Na_2CO_3} = \frac{5.3}{106} \times \frac{1000}{100 \times 10} = \frac{1}{2} = 0.5$$

$N = 0.5 \times 2$

$N_{Na_2CO_3} = 1.0$

$$M_{H_2C_2O_4 \cdot 2H_2O} = \frac{6.3}{120} \times \frac{1000}{100} = \frac{1}{2} = 0.5$$

$N = 0.5 \times 2$

$N = 1.$ Both N and M have same molarity and normality.

19. **(a, b, d)**

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{(m_1/M_1) + n_2} = \frac{n_2 M_1}{m_1 + n_2 M_1}$$

$$= \frac{(n_2/m_1)M_1}{1 + (n_2/m_1)M_1} = \frac{m}{1 + mM_1}$$

Matching Column Type

20. **(A → 5), (B → 3), (C → 4), (D → 2), (E → 1)**

(A) **Soda water** A solution of gas in liquid e.g., CO_2 in soft drinks.

(B) **Sugar solution** A solution of solid in liquid in which sugar particles (solid) are dissolved in water (liquid).

(C) **German silver** German silver is an alloy which is a solid solution of solid in solid. It is an alloy of Cu, Zn and Ni.

(D) **Air** A solution of gas in gas. Air is a mixture of various gases.

(E) **Hydrogen gas in palladium** is an example of solution of gas in solid. This is used as a reducing agent.

Integer Type

21. (2) At 1 bar pressure,

Partial pressure of O_2 $(p_{O_2}) = \dfrac{1}{5} \times 1$ bar $= 0.2$ bar

Partial pressure of N_2 $(p_{N_2}) = \dfrac{4}{5} \times 1$ bar $= 0.8$ bar

Applying Henry's law,

$p_{O_2} = K_H(O_2) \times x_{O_2}$ or $x_{O_2} = \dfrac{p_{O_2}}{K_H(O_2)}$

$p_{N_2} = K_H(N_2) \times x_{N_2}$ or $x_{N_2} = \dfrac{p_{N_2}}{K_H(N_2)}$

$$\therefore \quad \frac{x_{O_2}}{x_{N_2}} = \frac{p_{O_2}}{K_H(O_2)} \times \frac{K_H(N_2)}{p_{N_2}} = \frac{p_{O_2}}{p_{N_2}} \times \frac{K_H(N_2)}{K_H(O_2)}$$

$$= \frac{0.2 \text{ bar}}{0.8 \text{ bar}} \times \frac{6.60 \times 10^7 \text{ torr}}{3.30 \times 10^7 \text{ torr}} = \frac{1}{2}$$

i.e., $x_{N_2} : x_{O_2} = 2:1.$

22. (1) 5.37 M KOH solution means 5.37 moles of KOH are present in 1 litre of the solution.

But 5.37 moles of KOH = 5.37 × 56 g = 301.2 g

Thus, volume of solution containing 301.2 g KOH = 1000 mL

$\therefore$ Mass of solution containing 301.2 g of KOH

$= \dfrac{100}{30} \times 301.2 = 1004$ g

$\therefore$ Density of solution $= \dfrac{\text{Mass}}{\text{Volume}} = \dfrac{1004 \text{ g}}{1000 \text{ mL}} = 1.004$ g mL^{-1}.

Comprehension Type

23. (b) Henry's law is only applicable when the temperature is low.

24. (b) Hydrogen will have higher value of K_H because if gas has higher solubility, its K_H value is lower.

25. (a) Partial pressure of N_2 in air $(p_{N_2}) = p_{total} \times \chi_{N_2}$ (in air)

$= 5 \times 0.6$

p_{N_2} (in air) $= K_H \times \chi_{N_2}$ (in H_2O)

$5 \times 0.6 = 1.0 \times 10^5 \times \chi_{N_2}$ (in H_2O)

χ_{N_2} in 10 moles of water $= \dfrac{5 \times 0.6}{1.0 \times 10^5} = 3.0 \times 10^{-5}$

$$\chi_{N_2} = \frac{\eta_{N_2}}{\eta_{N_2} + \eta_{H_2O}}$$

$$3.0 \times 10^{-5} = \frac{\eta_{N_2}}{\eta_{N_2} + 10}$$

$\eta_{N_2} = 3 \times 10^{-4}$

DPP 2.2

Subjective Type

1. Both the components are appearing in the distillate and composition of liquid and vapour is same. This shows that

liquids have formed azeotropic mixture and boils at constant temperature, hence cannot be separated at this stage by distillation or fractional distillation. Solution having azeotropic nature show large positive or negative deviation from Raoult's law depending upon intermolecular interaction.

2. Mole fraction of cyclohexane = 0.32
∴ Mole fraction of ethanol = 1 – 0.32 = 0.68

Thus, $P_M = P^o_C \cdot X_C + P^o_E \cdot X_E$

$$P = 280 \times 0.32 + 168 \times 0.68 = 203.84 \text{ mm}$$

For the solution to be an ideal one, the vapour pressure should be 203.84 but the given value of vapour pressure is 376 mm, the solution is non-ideal.

3. $A: P_M = P'_B + P'_T = P^o_B \cdot X_B + P^o_T \cdot X_T$ | $X_B = \dfrac{1}{1+4}$

$= 160 \times \dfrac{1}{1+4} + 60 \times \dfrac{4}{1+4} = 32 + 48$ | $X_T = \dfrac{4}{1+4}$

$= 88$ mm

$$B: P_M = 160 \times \frac{w/78}{\frac{w}{78}+\frac{w}{92}} + 60 \times \frac{w/92}{\frac{w}{78}+\frac{w}{92}}$$

(Given, equal masses are mixed)

$$= 160 \times \frac{92}{170} + 60 \times \frac{78}{170} = 86.558 + 27.529 = 114.117 \text{ mm}$$

4. Given that,
Molar mass of $C_2H_4Br_2 = 188$, Molar mass of $C_3H_6Br_2 = 202$
Mass of $C_2H_4Br_2 = 60$ g, Mass of $C_3H_6Br_2 = 40$ g

$$P'_{C_2H_4Br_2} = P^\circ \times \text{Mole fraction of } C_2H_4Br_2 = 170 \times \frac{60/188}{\frac{60}{188}+\frac{40}{202}}$$

$$= 104.9 \text{ mm}$$

$$P'_{C_3H_6Br_2} = 127 \times \frac{40/202}{\frac{60}{188}+\frac{40}{202}} = 48.63 \text{ mm}$$

$P_M = 104.9 + 48.63 = 153.53$ mm.

5. In pure methanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them.

Therefore, the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules.

On the other hand, chloroform and acetone show –ve deviation from Raoult's law where the intermolecular attractive forces between the solute-solvent molecules are stronger than those between the solute-solute and solvent-solvent molecules.

Single Correct Answer Type

6. **(c)** $P^o_A X_A = P_T \cdot Y_A$

$$\therefore \frac{X_A}{Y_A} = \frac{P_T}{P^o_A} < 1 \qquad (\because P_T < P^o_A)$$

$X_A < Y_A$.

7. **(c)** $P_M = P^o_{C_5H_{12}} \cdot X^o_{C_5H_{12}} + P^o_{C_6H_{14}} \cdot X_{C_6H_{14}}$

Thus, $P_M = 440 \times \dfrac{1}{4} + 120 \times \dfrac{4}{5} = 184$

Now, $P_{C_5H_{12}} = P^o_{C_5H_{12}} \cdot X_{C_5H_{12}(\ell)} = P_M \cdot X_{C_5H_{12}(g)}$

$\therefore \quad 440 \times \dfrac{1}{5} = 184 \times X_{C_5H_{12}(g)}$

$\therefore \quad X_{C_2H_{12}(g)} = 0.478.$

8. **(d)** $P_M = 80 \times \dfrac{3}{5} + 60 \times \dfrac{2}{5}$

$= 48 + 24 = 72$ torr

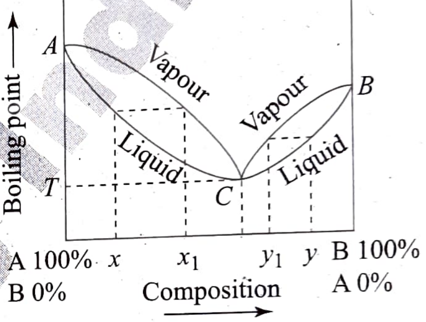
9. **(a)** A characteristic of azeotropes.

10. **(b)** Substances of high vapour pressure (e.g., gasoline) evaporates more quickly than substances of low vapour pressure (e.g., motor oil).

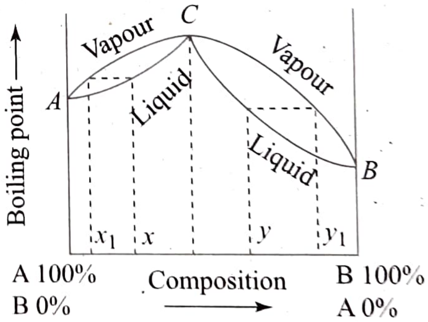
11. **(b)** Lower is the b.p. of solvent more is its vapour pressure.

12. **(a)** If $X_A = 0$, then pure B $P^o_B = 138$
If $X_A = 1$, then pure A $P^o_A = 120 + 138 = 258$

13. **(b)**



Non-ideal solution with positive deviation



Non-ideal solution with negative deviation

14. **(a)** $P_{Total} \times y_A = P_A$

$$\frac{1}{P_{Total}} = y_A \times \frac{1}{P_A}$$

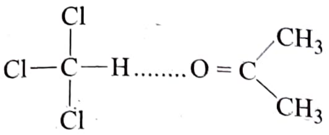
When $\dfrac{1}{P_{Total}}$ is plotted against y_A, we get straight line passi through origin having slope of $\dfrac{1}{P_A}$.

Multiple Correct Answers Type

15. **(a, b, d)**
Benzene and toluene mix to form an ideal solution.

16. **(b, c, d)**
For a reaction to take place ΔG must be negative.

17. **(a, b, d)**
When $CHCl_3$ and $(CH_3)_2CO$ are mixed, the hydrogen bonding takes place between the two molecular species due to which the escaping tendency of either of the liquid molecules become less. Consequently, the boiling point of solution increases.



Hydrogen bonding between chloroform and acetone.

18. **(b, c)**
Azeotrope is a type of liquid mixture, having a definite composition, and boiling like a pure liquid.

19. **(a, b, c)**
Boiling point of $CCl_4 <$ that of $SiCl_4$. The vapour must always be richer in more volatile component. Hence, the upper curve represents the composition of the vapour and the lower curve represents the composition of the solution at the corresponding boiling point.

Matching Column Type

20. **$(A \rightarrow p, r), (B \rightarrow q), (C \rightarrow p, r), (D \rightarrow s)$**
For solution showing positive deviation from ideal behaviour, ΔH and ΔV both are positive. So, mixing is endothermic.

Integer Type

21. (4)

$$p_w = 733 \text{ mm}$$
$$p_N = 27 \text{ mm}$$
$$p_w = p_w^o \cdot x_w$$
$$733 = 760 \cdot x_w$$
$$x_w = \frac{733}{760} = 0.964$$
$$x_N = 0.036$$
$$x_w = \frac{n_N}{n_w + n_N}$$
$$\frac{x_w}{x_N} = \frac{n}{n_N}$$
$$\frac{0.964}{0.036} = \frac{w_w \times 123}{18 \times w_N}$$
$$\frac{w_w}{w_N} = \frac{3.89}{1} \approx 4$$

22. (2)

$$p_M = p_A^o \cdot x_A + p_B^o \cdot x_B$$
$$= 50 \times \frac{1}{2} + 100 \times \frac{1}{2}$$
$$= 25 + 50 = 75$$

Now, $p_A = p_A^o \cdot x_A\,(l) = p_M \times x_A\,(g)$

$$= 50 \times \frac{1}{2} = 75 \times x_A\,(g)$$
$$x_A\,(g) = \frac{1}{3}$$
$$x_B\,(g) = \frac{50}{75} = \frac{2}{3}$$
$$\frac{x_B(g)}{x_A(g)} = \frac{2 \times 3}{3 \times 1} = 2.$$

Comprehension Type

23. **(b)** Partial pressure of Toluene $P_t = P_t^0 \times X_A$

$$= 4.274 \times \frac{1}{1+1} = 2.137$$

Partial pressure of Benzene $P_b = P_b^0 \times X_B$

$$= 13.734 \times \frac{1}{1+1} = 6.867$$
$$P_T = P_t + P_b = 2.137 + 6.867$$
$$\boxed{P_T = 9.004 \text{ KN/m}^2}$$

It is the partial pressure of solution and at this pressure the first vapour forms.

24. **(a)** $X_T = \dfrac{0.5 \times 4.74}{0.5 \times 4.274 + 0.5 \times 13.734} = 0.237$

25. **(b)** $P = 0.5 \times 4.274 + 0.5 \times 13.734 = 9.004 \text{ KN/m}^2$

26. **(b)** $0.5 = \dfrac{x_T \times 13.734}{4.274(1 - x_T)} + x_T \times 13.734$

$$\Rightarrow \quad X_T = 0.7627$$

DPP 2.3

Subjective Type

1. NaCl is a non-volatile solute. So, its addition to water lowers the vapour pressure of the water. Hence, boiling point of water (solution) increases. Whereas methyl alcohol is more volatile than water.
So, its addition to water increases the total vapour pressure over the solution. It results in the decrease of boiling point.
2. When glucose (non-volatile solute) is dissolved in water, the rate of evaporation of water decreases because some fraction of surface is covered by glucose molecules. Moreover, according to Raoult's law:
$$p = p^o x_A$$
x_A = mole fraction of solvent in the solution
Vapour pressure of solution (p) will be less than that of pure solvent (p^o).
3. (i) The solution containing solute B will show greater elevation in the boiling point because $\Delta T_b \propto \dfrac{1}{Mw}$.

(ii) $\Delta t_b = (101.24 - 100.00)°C = 1.24°C$

$$m = \frac{\Delta t_b}{K_b} = \frac{1.24°C}{0.512°C/m} = 2.42 \text{ m}$$
$$M = \frac{288 \text{ g}/90.0 \text{ g water}}{2.42 \text{ mol}/1000 \text{ g water}} = 400 \text{ g/mol}$$

The weight of a molecule is 1320 u. If the value of n were 1, corresponding to CH_2O, the weight would be 30 u. Hence n must be 1320/30 = 44, and the molecular formula is $C_{44}H_{88}O_{44}$.

4. (a) We have, $\frac{P^o - 21.85}{21.85} = \frac{30 \times 18}{90 \times m}$ for case I ..... (1)

Now, mass of solvent = 90 + 18 = 108 g

$$\frac{P^o - 22.15}{22.15} = \frac{30 \times 18}{108 \times m} \quad \text{for case II ...... (2)}$$

$\therefore$ By Eq. (1) $P^o_M - 21.85 \text{ m} = 21.85 \times 6 = 131.1$

By Eq. (2) $\underset{-}{P^o_M} \underset{+}{-\,22.15} = \underset{-}{22.15 \times 5} = 110.75$

$\therefore$ $0.30 \text{ m} = 20.35$

$\therefore$ $m = \frac{20.35}{0.30} = 67.83 \text{ g mol}^{-1}$

(b) On substituting the value of m in Eq. (1),

$$\frac{P^o - 21.85}{21.85} = \frac{30 \times 18}{90 \times 67.83}$$

$\therefore$ $P^o = 23.78$ mm

5. According to Raoult's law:

$$\frac{P^o - P_s}{P_s} = \frac{w}{m} \times \frac{M}{W}$$

Given if $P^o = 100$, then $P_s = 75$ mm, $m = 60$, M = 18, W = 100 g

$$\frac{100 - 75}{75} = \frac{w \times 18}{60 \times 100}$$

$\therefore$ $w = 111.11$ g

Also, molality of solution

$$= \frac{\text{Mass of solute}}{\text{Molar mass of solute} \times \text{mass of solvent (in kg)}}$$

$$= \frac{111.11}{60 \times \frac{100}{1000}} = 18.52 \text{ m}$$

Single Correct Answer Type

6. (c) $\Delta T_b = \frac{1000\, K'_b \times w}{m.W}$; if $w/m = 1$, $W = 1000$ g,

$\Delta T_b = K'_b$

7. (b) $\frac{P^o - P_s}{P_s} = \frac{n}{N} = \frac{w \times M}{m \times W}$

or $\frac{P^o - \frac{95}{100}P^o}{\frac{95}{100}P^o} = \frac{w \times 0.3 \text{ m}}{W \times m} (M = 0.3 \text{ m})$

or $\frac{W}{w} = 5.7$

8. (a) $\Delta T = \frac{1000 \times K_b \times n \times M}{W \times M} = \frac{1000 \times K_b \times n}{N \times M}$

or $\frac{n}{N} = \frac{\Delta T \times M}{1000 \times K_b} = \frac{0.6 \times 18}{1000 \times 0.52} = 0.02$

$\therefore$ $\frac{N}{n} = 50$ or $1 + \frac{N}{n} = 51$

$\therefore$ $\frac{n + N}{n} = 51 \quad \therefore \quad \frac{n}{n + N} = 0.02$

9. (b) $T_S = 372.6$ K for water since 1 bar < 1 (1 bar = 0.998 atm).

10. (b) $\Delta T = K_b \times \frac{w_B \times 1000}{m_B \times w_A} = K_b \times \frac{Y \times 1000}{M \times 250} = \frac{4K_bY}{M}$

11. (b) $\frac{10 - 9}{10} = \frac{\frac{1}{x}}{\frac{1}{x} + \frac{20}{200}}$

$$\frac{1}{10} = \frac{\frac{1}{x}}{\frac{1}{x} + \frac{1}{10}} = \frac{10}{x + 10} \Rightarrow x = 90$$

12. (a) $K_b = \frac{R \times (T_b)^2}{1000 \times L_v} \quad (L_v = 40)$

$$= \frac{8.31 \times (273)^2}{1000 \times 40}$$

$= 0.512$ K kg/mol

13. (c) $\Delta T_b = K_b \times m$

Hence, molality, $m = \frac{\Delta T_b}{K_b} = \frac{0.52}{0.52} = 1$

Molality = 1 means 1 mole of solute in 1000 g of solvent.
But 1000 g of solvent (Water)

$$= \frac{1000}{18} \text{ moles} = 55.55 \text{ moles}$$

$\therefore$ Mole fraction of urea = $\frac{1}{1 + 55.55} = 0.018$.

Multiple Correct Answers Type

14. (b, c)
Common salt is a non-volatile solute.

15. (a, c)
Vapour pressure of solution = Vapour pressure of solvent in solution.

16. (a, b)
If P^0 is the vapour pressure of pure solvent and P_S is the vapour pressure of the solution, the difference $(P^0 - P_S)$ is termed lowering in vapour pressure and the ratio $\left[\frac{P^0 - P_S}{P^0}\right]$ is termed relative lowering in vapour pressure.
According to Raoult's law:

$$\frac{P^0 - P_S}{P^0} = \frac{N_1}{N_1 + N_2}$$

For very dilute solution, $N_1 \lll N_2$, therefore $\frac{(P^0 - P_S)}{P_S} = \frac{N_1}{N_2}$.

17. (b, c)
Vapour pressure of solution containing non-volatile solute is always smaller than that of solvent points, a and b represent the boiling points of solvent and solution respectively (temperatures

at which their V.P. = 1 atm each). Hence gap $ab = K_b m$ = elevation of boiling point.

18. **(b, c, d)**

$K_b = \dfrac{RT_b^{o2}M}{1000\Delta H}$ where T_b^o = boiling point of solvent, ΔH = molar enthalpy of vaporisation and M = molar mass of solvent

Matching Column Type

19. **(A → q), (B → p), (C → s), (D → r)**
    (a) Loss in mass of solution ∝ V.P. of solution (p_s)
    (b) Loss in mass of solvent α Difference of V.P. of solvent and solution, i.e., ($p^\circ - p_s$).
    (c) Since the air is saturated at the V.P. of solvent, so total loss $(w_1 + w_2) \propto p^\circ$.
    (d) Relative lowering of V.P. = $\dfrac{p^o - p_s}{p^o} = \dfrac{w_2}{w_1 + w_2}$

Integer Type

20. **(4)** $p_s = 80\%$ of p°

$$\frac{p^\circ - p^s}{p^\circ} = x_B$$

$$\frac{p^\circ - 0.80\,p^\circ}{p^\circ} = \frac{n}{n+N}$$

$$0.20 = \frac{n}{n+N}$$

$$\frac{1}{0.20} = \frac{n+N}{n} = 1 + N/n$$

$$\frac{N}{n} = \frac{1}{0.20} - 1 = \frac{0.80}{0.20} = 4.$$

21. **(5)**

$p_s = 20\%$ of p°, Solute = $\dfrac{w}{40}$ mol, Solvent (octane) = $\dfrac{57\text{ g}}{114\text{ g/mol}}$ = 0.5 mol

Now, $\dfrac{p^\circ - p^s}{p^\circ} = x_B$

$$\frac{p^\circ - 0.20p^\circ}{p^\circ} = \frac{w/40}{w/40 + 5}$$

$$0.20\left(\frac{w}{40} + 0.5\right) = \frac{w}{40}$$

$$0.20w + 0.20 \times 0.5 \times 40 = w$$

$$4 = 0.80\,w$$

$$w = 5\text{ g}.$$

Comprehension Type

22. **(a)** $\Delta T_b = k_b \times m$

K_b = molal elevation constant

$$\lim_{m \to 0} \frac{\Delta T_b}{m} = K_b.$$

23. **(d)** $\Delta T_b = m \times K_b$

$K_b = 0.52°\text{ mol}^{-1}\text{ kg}$

$$0.52 = 0.52 \times 3$$

$$m = 1$$

$$\frac{w}{m \times W} = 1$$

$$\frac{w}{m} = 1 \times 1000 \Rightarrow w = 1000\text{ g}$$

$$n = \frac{w}{m} = 1000$$

$$N = \frac{W}{M} = \frac{1000}{18}$$

$$X_A = \frac{n}{N+n} = \frac{1000}{\frac{1000}{18} + 1000} = \frac{1000 \times 18}{1000 \times 18 \times 1000}$$

$$= 0.018$$

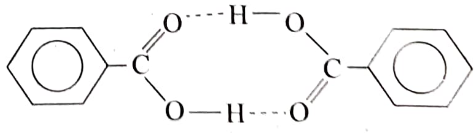
DPP 2.4

Subjective Type

1. When salt is spread over snow covered roads, snow starts melting from the surface because depression of freezing point of water takes place due to addition of salt. It helps in clearing of roads. Hence, the phenomena is depression in freezing point which helps in clearing the snow covered roads in hilly areas.
2. A given mass of methyl alcohol, because it has a lower molecular weight, contains more moles than the same mass of glycerine. More moles of solute means higher molality and thus lower freezing point. It would take less methyl alcohol to protect a radiator to a given freezing point.
3. The freezing point depression constant is so large that an accurate freezing point depression can be obtained on a solution with very few moles dissolved per kilogram of camphor. Thus, high molecular weight materials give measurable freezing point depressions in this solvent. However, there is a problem in getting many materials to dissolve in camphor.
4. $m = \dfrac{\Delta t}{K_f} = \dfrac{(5.5 - 3.1)^\circ\text{C}}{5.12^\circ\text{C/m}} = 0.47\text{ m}$

$$m = \frac{\Delta t}{K_b} = \frac{(82.6 - 80.1)^\circ\text{C}}{2.53^\circ\text{C/m}} = 0.99\text{ m}$$

It is evident that the number of moles of solute particles at the boiling point is twice that at the freezing point of the solution. In fact, benzoic acid dimerizes (forms double molecules) by hydrogen bonding at the lower temperature, but the dimmers are broken up at the elevated temperature.



Single Correct Answer Type

5. **(a)** K_f is characteristic constant for a given solvent.
6. **(c)** ∵ $\Delta T = K_f \times$ molality

59 g solution has 9 g glucose and 50 g water.

$$\therefore \quad \Delta T = K_f \times \frac{\frac{9}{180 \times 50}}{1000} = K_f.$$

7. (c) $\Delta T = K_f \times \dfrac{w_B \times 1000}{m_B \times w_A}$

$$0.186 = 1.86 \times \frac{w_B \times 1000}{60 \times 500}$$

$w_B = 3$ g.

8. (b) $\Delta T_f = K_f \times$ molality

$\Delta T_b = K_b \times$ molality

$$\therefore \quad \Delta T_b = \frac{K_b}{K_f} \times \Delta T_f = \frac{0.512}{1.86} \times 0.186 = 0.0512°C$$

9. (a) $\therefore \Delta T = \dfrac{1000 \times K'_f \times w}{W.m}$

$$9.3 = \frac{1000 \times 1.86 \times 50}{62 \times W}$$

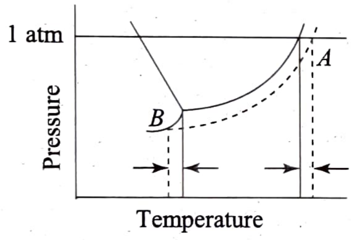
$\therefore \quad W = 161.29$

$\therefore$ Ice separated = 200 – 161.29 = 38.71 g

10. (a) $\Delta T = K_f \times \dfrac{w_B \times 1000}{m_B \times w_A} = 1.86 \times \dfrac{17 \times 1000}{46 \times 1000} = 0.69$

$\therefore$ Freezing point of solution = 0 – 0.69 = – 0.69°C.

11. (d)

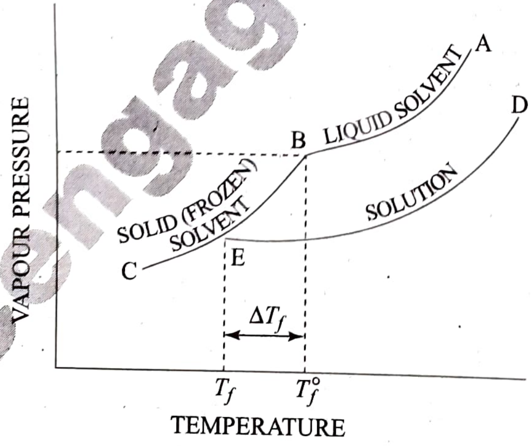


Point A represents the elevation of boiling point and point B represent the depression in freezing point.

$$\left.\begin{array}{l} A = \Delta T_b \\ B = \Delta T_f \end{array}\right\}$$

Multiple Correct Answers Type

12. (a, d)
The facts are clear from the following figure.



Depression in freezing point

13. (a, c, d)

$\Delta T_b = K_b \times m$

$\therefore \quad 0.18 = 0.512 \times m$

$\Delta T_f = K_f \times m$

$$= 1.86 \times \frac{0.18}{0.512} = 0.654$$

$\therefore \quad T_f = -0.654°C$

14. (b, c, d)
KI reacts with HgI_2 to form a complex as

$$2KI + HgI_2 \rightarrow K_2[HgI_4] \xrightarrow{\text{ionizes}} \underbrace{2K^+ HgI_4^{2-}}_{\text{3 ions}}$$

$$\underbrace{(2K^+ + 2I^-)}_{\text{3 ions}}$$

Thus, number of ions decreases in the solution. Hence, depression in freezing is less, i.e., actual freezing point is raised.

15. (c, d)
Elevation in boiling point and depression in freezing point are linked to the lowering of vapour pressure by a non-volatile solute.

Matching Column Type

16. (A → r, s), (B → p, q), (C → r, s), (D → p, q)

(a) $K_f = \dfrac{RT_f^{o\,2}}{1000L_f} = \dfrac{RT_f^{o\,2} M}{1000\Delta H_f}$

T_f^o (water) = 273K. M = 18

(b) $K_b = \dfrac{RT_b^{o\,2}}{1000L_v} = \dfrac{RT_b^{o\,2} M}{1000\Delta H_f}$

T_b^o (water) = 373K. M = 18

(c) $\Delta T_f = K_f \times m = K_f \times \dfrac{9 \times 1000}{180 \times 50} = K_f$

(d) $\Delta T_b = K_b \times m = K_b \times \dfrac{3 \times 1000}{60 \times 50} = K_b$

Integer Type

17. (8) The given values are:

$K_f = 4.90$ K kg mol^{-1}

$W_{solute} = 3.26$ g

$W_{solvent} = 226$ g

$\Delta T_f = 0.112°C$

Now, molecular mass can be calculated as:

$$Mw_{solute} = \frac{K_f \times W_{solute} \times 1000}{W_{solvent} \times \Delta T_f}$$

$$= \frac{4.901 \times 3.26 \times 1000}{226 \times 0.112} = 632 \text{ g mol}^{-1}$$

Now, molecular mass of $Se_x = x \times 78.8$

$632 = x \times 78.8$

or $\quad x = \dfrac{632}{78.8} = 8$

18. (5) Here, mass of solute = 6.2 g

$\Delta T_f = 3.72°C$

M. mass of solute $(CH_2OH)_2 = 62$

$$M_2 = \frac{1000 \times K_f \times w_2}{w_1 \cdot \Delta T_f}$$

$$w_1 = \frac{1000 \times K_f \times w_2}{M_2 \cdot \Delta T_f} = \frac{1000 \times 1.86 \times 6.2}{62 \times 3.72} = 50\,g$$

Ice that will separate out = 55 – 50 = 5 g.

Comprehension Type

9. (d) $$\frac{p^o - p_s}{p^o} = \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1}$$

i.e., $$\frac{0.024 - p_s}{0.024} = \frac{68.4/342}{1000/18}$$

or $$\frac{1000}{18}(0.024 - p_s) = \frac{68.4}{342} \times 0.024$$

or $0.024 - p_s = 0.000086$ or $p_s = 0.0239$ atm

20. (c) $\Delta T_f = K_f \times m = 1.86 \times \dfrac{68.4}{342} = 0.372°$

$\therefore$ Freezing point of the solution = –0.372°C

DPP 2.5

Subjective Type

1. Given that, $w = 2.5$ g, $V = \dfrac{200}{1000}$ litre, $\pi = \dfrac{60}{76}$ atm,

$T = 288$ K

$$\because \quad \pi V = \frac{w}{m} ST = \frac{60}{76} \times \frac{200}{1000} = \frac{25}{m} \times 0.0821 \times 288$$

$\therefore \quad m = 374.38$ g mol^{-1}

Also, $$\frac{\pi_1}{\pi_2} = \frac{T_1}{T_2}$$

$$\therefore \quad \frac{60}{\pi_2} = \frac{288}{298}$$

$\therefore \quad \pi_2 = 62.08$

2. $\pi_1 V_1 = \dfrac{w_1}{m_1} ST_1$ for urea

$\pi_2 V_2 = \dfrac{w_2}{m_2} ST_2$ for sugar

Since, 100 mL of urea solution are mixed with 100 mL of cane-sugar solution and thus, total volume becomes 200 mL in which 3.4 g urea and 1.6 g sugar is present.

$$\therefore \quad \pi_1 \times \frac{20}{1000} = \frac{3.4}{60} \times 0.0821 \times 293$$

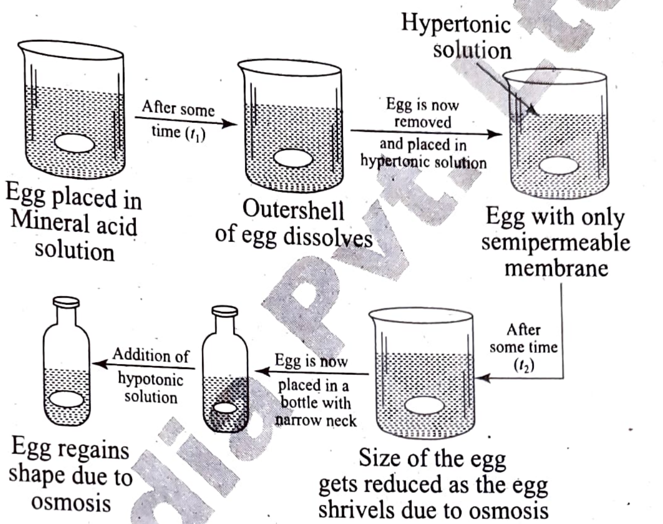
$\pi_1 = 6.82$ atm

$$\therefore \quad \pi_2 \times \frac{20}{1000} = \frac{1.6}{342} \times 0.0821 \times 293$$

$\therefore \quad \pi_2 = 0.56$ atm

$\therefore \quad \pi_{Total} = \pi_1 + \pi_2 = 6.82 + 0.56 = 7.38$ atm.

3. When egg is placed in mineral acid solution, outershell of egg gets reduced and egg shrivels due to osmosis. Egg is now placed in a bottle with narrow neck. Finally on adding hypotonic solution egg regain its shape due to osmosis. Diagrammtically it can be represented as:


Hypertonic solution
Egg placed in Mineral acid solution
After some time (t_1)
Outershell of egg dissolves
Egg is now removed and placed in hypertonic solution
Egg with only semipermeable membrane
After some time (t_2)
Size of the egg gets reduced as the egg shrivels due to osmosis
Egg is now placed in a bottle with narrow neck
Addition of hypotonic solution
Egg regains shape due to osmosis

4. (i) Because when an unripe mango is placed in a concentrated salt solution to prepare pickle, then mango loose water due to osmosis and get shrivelled.

(ii) The osmotic pressure is equal to that of a column of the solution 2.4 mm high.

π = (height) (density) (g)

= $(2.4 \times 10^{-3}$ m$)(0.88 \times 10^3$ kg/m$^3)$ $(9.81$ m/s$^2) = 20.7$ Pa

The molar concentration can now be determined from the osmotic pressure equation.

$$M = \frac{\pi}{RT} = \frac{20.7\ \text{N/m}^2}{(8.314\ \text{J/K mol})\ (298\ \text{K})}$$

$$= 8.3 \times 10^{-3}\ \text{mol/m}^3 = 8.3 \times 10^{-6}\ \text{mol/L}$$

The solution contained 0.20 g solute/100 mL solution, or 2.0 g/L, and has been found to contain 8.3×10^{-6} mol/L. Then

$$MW = \frac{2.0\ \text{g}}{8.3 \times 10^{-6}\ \text{mol}} = 2.4 \times 10^5\ \text{g/mol}$$

Single Correct Answer Type

5. (d) In osmosis only solvent particles move.

6. (b) $$\pi = \frac{CRT}{V} = \frac{wRT}{m.V_{\text{in L}}} = \frac{w \times RT \times 1000}{m \times V_{\text{in mL}}}$$

$$\pi = \frac{1000\ RT}{m} \times C_{g/cm^3}$$

$$\therefore \quad \text{slope} = \frac{1000\ RT}{m} = 2 \times 10^{-3}$$

$$\therefore \quad m = \frac{1000 \times 0.0821 \times 300}{2 \times 10^{-3}} = 1.23 \times 10^7\ \text{g mol}^{-1}$$

7. (d) For ternary electrolyte;

$P_1 = CST = 0.05 \times 3 \times S \times T$;

For B; $2P = 0.1 \times S \times T$

$\therefore \quad P_1 = 3P$

8. (d) $\pi V = \frac{w}{m} ST$

∴ $\pi = \frac{w}{V} \cdot \frac{ST}{m}$

$\pi = c' \cdot \frac{ST}{m}$ (c' is in g/litre).

The plots of π vs. c (g/cm^3) have slope = $\frac{ST \times 1000}{m}$

∴ $\frac{ST \times 1000}{m} = 4.65 \times 10^{-3}$

$m = \frac{0.0821 \times 293 \times 1000}{4.65 \times 10^{-3}} = 5.17 \times 10^{6}$

9. (d) $KCl \rightleftharpoons K^+ + Cl^-$

Osmosis is a colligative property and thus, osmolarity of 0.2 M KCl = 0.4 M.

10. (b) Low concentration solution (0.05 M $BaCl_2$) will flow towards the high concentration solution (0.1 M NaCl) is called osmosis.

Multiple Correct Answers Type

11. (c, d)

The solute molecules or ions cannot pass through the semipermeable membrane, only the solvent molecules can pass through. Hence no precipitation is formed on either side.

$M_{\text{effective}}$ ($AgNO_3$) = iC = 2 × 0.1 = 0.2

$M_{\text{effective}}$ ($BaCl_2$) = iC = 3 × 0.1 = 0.3

Osmosis occurs from $AgNO_3$ side to $BaCl_2$ side.

12. (c, d)

$Cu_2[Fe(CN)_6]$ acts as semipermeable membrane only for aqueous solutions.

13. (b, d)

From PV = nRT it is clear that if V is constant $P \propto T$ and if T is constant PV is constant.

14. (a, b, c)

$\pi = CRT = \frac{w}{V}\frac{RT}{m}$ $\quad \pi = C \text{ (in g/mL)} \frac{RT}{m}$

∴ slope = $\frac{RT}{m} = 4.65 \times 10^{-3} \times 10^{-3}$ (in g/L)

∴ $m = \frac{0.0821 \times 300}{4.65 \times 10^{-6}} = 5.3 \times 10^{6}\ \text{g mol}^{-1}$

15. (a, b, d)

$\pi = CRT$

Comparing with $y = mx + c$

Slope = RT

Matching Column Type

16. **(i → d), (ii → c), (iii → a), (iv → b), (v → f), (vi → e)**

Column II defines Column I.

Integer Type

17. (2) $\pi = \frac{n}{V} RT$

$\pi = \frac{w}{MV} RT$

$\pi = \frac{dRT}{M} \Rightarrow d = \frac{\pi M}{RT} = \frac{0.2 \times 240}{0.08 \times 300} = 2$

18. (5) $\pi V = (n_1 + n_2)RT$

$\pi V = \left(\frac{w_1}{M_1} + \frac{w_2}{M_2}\right) RT$

$\pi \times 1 = \left(\frac{18}{180} + \frac{6}{60}\right) \times 0.0821 \times 300$

$\pi = 4.926 \text{ atm} \approx 5 \text{ atm}.$

Comprehension Type

19. (d) No blue colour formation because 0.1 M $[K_4Fe(CN)_6]$ solvent molecules move through SPM to 0.1 M $FeCl_3$. So no reaction between it.

20. (b) By applying external pressure in which side that have concentration low (hypotonic) or side '*y*' osmosis can be stopped by it.

DPP 2.6

Subjective Type

1.

$CaCl_2$	→	Ca^{2+}	+	$2Cl^-$
Before dissociation	1	0		0
After dissociation	$(1 - \alpha)$	α		2α

Given, w = 20 g, V = 100 mL, T = 273 K

Formula mass of $CaCl_2$ = 111 g mol^{-1}

$$\pi_N = \frac{w}{m.V} \times S \times T = \frac{20 \times 1000 \times 0.0821 \times 273}{111 \times 100} = 40.38 \text{ atm}$$

Now, $\frac{\pi_{\text{exp}}}{\pi_N} = 1 + 2\alpha = 1 + 2 = 3 \qquad \because \alpha = 1$

∴ $\pi_{\text{exp}} = 40.38 \times 3 = 121.14$ atm.

2. (a) When the solute does not undergo any dissociation or association in the solution i.e., for non-electrolyte solutes.

(b) When the solute undergoes association in the solution.

(c) When the solute undergoes dissociation in the solution.

3. If the solution is concentrated, the particle begins to interact with each other as much as with solvent. This obviously means that the vapour pressure starts to depend on the nature of the solute, and not just on the number of solute particles. Hence, to get the accurate values of molar mass the solution should be very dilute.

4. Let the degree of dimer formation be α. The reaction occurs as under:

	$2A$	$\rightleftharpoons$	$(A)_2$
Initially	m		0
After dimer formation	$m - m\alpha$		$\frac{m\alpha}{2}$

where m = molality = molarity (as also given)

Due to dimer formation, the resultant Molality will be

$= (m - m\alpha) + \frac{m\alpha}{2}$

van't Hoff factor, $i = \frac{(m - m\alpha) + \frac{m\alpha}{2}}{m}$

$$i = \frac{m\left(1 - \frac{\alpha}{2}\right)}{m} \Rightarrow i = 1 - \frac{\alpha}{2}$$

As we know the elevation in boiling point

$$\Delta T_b = K_b \times i \times C_m$$

$$\Rightarrow \quad = K_b \times \left(1 - \frac{\alpha}{2}\right) \times m, \text{ here } C_m = m$$

$$\Rightarrow \quad \alpha = \frac{2(K_b m - \Delta T_b)}{K_b m}$$

The equilibrium constant for dimer formation is

$$K_{eq} = \frac{[A_2]}{[A]^2} = \frac{m\frac{\alpha}{2}}{\{m(1-\alpha)\}^2} = \frac{m\frac{\alpha}{2}}{m^2(1-\alpha)^2}$$

$$= \frac{\alpha}{2m(1-\alpha)^2} \qquad \text{(i)}$$

Putting the value of α in equation (i)

$$K_{eq} = \frac{2(K_b m - \Delta T_b)}{K_b m}$$

$$= \frac{\dfrac{2(K_b m - \Delta T_b)}{K_b m}}{2m\left\{1 - \dfrac{2(K_b m - \Delta T_b)^2}{K_b m}\right\}} = \frac{K_b(K_b m - \Delta T_b)}{(2\Delta T_b - K_b m)^2}$$

Single Correct Answer Type

5. (d) On dissociation, number of particles increases, thus $i > 1$ on association, number of particles decreases thus $i < 1$.

6. (c) $Na_2SO_4 = 2Na^+ \; SO_4^{2-}$

$$\begin{array}{ccc} 1 & 0 & 0 \\ 1-\alpha & 2\alpha & \alpha \end{array}$$

where α is degree of dissociation

$$\therefore \quad i = 1 - \alpha + 2\alpha + \alpha = 1 + 2\alpha$$

7. (a) $A_xB_y \rightarrow xA^{y+} + yB^{x-}$

$$\begin{array}{ccc} 1-\alpha & x\alpha & y\alpha \end{array}$$

$$i = 1 - \alpha + x\alpha + y\alpha$$

$$\alpha = \frac{i-1}{(x+y-1)}$$

8. (d) Depression in freezing point, $\Delta T_f = K_f m$ (where, m = molality)

$$= 5.12 \times \frac{0.223 \times 1000}{4.4 \times 136} = 1.91$$

$\therefore$ Theoretical $\Delta T_f = 1.91$

Actual $\Delta T_f = 5.3°C - 4.4°C = 0.83°C$

$$\therefore \quad i = \frac{0.83}{1.91} = 0.43$$

$$\because \quad i < 1$$

$\therefore$ Association will take place.

Thus, it can be said that phenylacetic acid dimerises in benzene.

9. (d) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$i = 1 + (y-1)x = (1 + x)$$

$$x = \frac{D-d}{d} = \frac{104.25 - 100}{100} = \frac{4.25}{100} = 0.0425$$

$$\therefore \quad i = 1 + x = 1.0425$$

where (D = theoretical V.D. = $\frac{\text{molar mass}}{2}$

d = experimental V.D.)

10. (b) van't Hoff factor is the measurement of total number of ions present in the solution. Therefore greater the concentration of solution greater will be its van't Hoff factor.

Concentration NaCl	
A. 0.1 M B. 0.01 M C. 0.001 M	On moving top to bottom • Concentration decreases • van't Hoff factor (i) decreases

11. (a) $i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$

$$= \frac{164}{65.6} = 2.5$$

$$a = \frac{i-1}{n-1}, \qquad n = 3 \text{ (number of ions)}$$

$$= \frac{2.5-1}{3-1} = \frac{1.5}{2} = 0.75$$

$\therefore$ Percentage ionization of MX_2 will be 75%.

Multiple Correct Answers Type

12. **(a, c)**
   (a) The total conc. of species in $MgCl_2$ solution will be 0.3 M and in NaCl solution it will be 0.2 M. Glucose is a non-electrolyte, hence concentration of glucose solution will be 0.1 M.
   (b) Density is defined as mass per unit volume and the volume of the solution varies with temperature.
   (d) In solution, $K_4Fe(CN)_6$ ionizes as $K_4Fe(CN)_6 \rightarrow 4K^+ + Fe(CN)_6^{4-}$. Hence, the limiting value of van't Hoff factor will be 5.

13. **(a, b, c)**

Osmolarity of solution $X = 2 \times 0.1 = 0.2$ ($i = 2$)

van't Hoff factor for

$$Y = 1 - \left(1 - \frac{1}{n}\right)\alpha = 0.5 \; (n = 2; \alpha = 1)$$

Osmolarity of solution $Y = 0.5 \times 0.1 = 0.05$

14. **(a, b, c)**

Since the solute X behaves as univalent electrolyte in solution, so for this solute, $i = 2$.

Since the solute Y dimerises in solution, so for this solute $i = \frac{1}{2}$.

We know that

b.p. ∝ i, ∴ b.p. of X will be greater than that of Y.

Osmotic pressure $\propto \frac{1}{i}$ $\qquad \therefore$ f.p. of X > o.p. of Y

Freezing point $\propto \frac{1}{i}$; ∴ f.p. of X < f.p. of Y and relative lowering of V.P. i.e., $\frac{\Delta P}{P^o} \propto i$

$$\therefore \quad \left(\frac{\Delta P}{P^o}\right)_X > \left(\frac{\Delta P}{P^o}\right)_Y$$

Thus statement (d) is incorrect. All other statements are correct.

15 **(a, b, c, d)**

$$\text{Molarity} = \frac{1.2575 \times 1000}{251.5 \times 250} = 0.02 \text{ M}, \pi = CST$$

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$\therefore \quad \pi_{\text{obse.}} = 0.02 \times 0.0821 \times 300 = 0.4926 \text{ atm} = 374.38 \text{ mm.}$

$$\frac{\pi_{\text{obse}}}{\pi_{\text{cal}}} = i = \frac{1.478 \times 760}{374.38} = 3$$

$\because \quad \alpha = \dfrac{i-1}{n-1}$ and $\alpha = 1, \qquad \therefore n = 3$

Also,

$$\begin{array}{llccc} & [Cr(NH_3)_6]SO_4{\times}Cl \rightleftharpoons & [Cr(NH_3)_6^{3+}] + & SO_4^{2-} + & Cl^- \\ & 0.02 & 0 & 0 & 0 \\ \text{Eq. conc.} & 0 & 0.02 & 0.02 & 0.02 \end{array}$$

16. (a, c, d)

$CrCl_3 \cdot 6H_2O$

$\pi = CST \cdot (1 - \alpha + x\alpha + y\alpha)$

$98.52 = 1 \times 0.0821 \times 300 \times (x + y)(\alpha = 1)$

$\therefore \quad (x + y) = 4$

$\therefore$ $CrCl_3 \cdot 6H_2O$ can be written as:

$$\begin{array}{ccc} [Cr(H_2O)_6]Cl_3 \rightleftharpoons & [Cr(H_2O)_6]^{3+} + & 3Cl^{-1} \\ 1 & 0 & 0 \\ 1-\alpha & \alpha & 3\alpha \end{array}$$

3 mole of $AgNO_3$ will react with 1 mole of $Cr(H_2O)_6Cl_3$.

$$\begin{array}{lcccc} & Cr(H_2O)_6Cl_3 + & 3AgNO_3 \longrightarrow & [Cr(H_2O)_6](NO_3)_3 + & 3AgCl \\ \text{Mole} & 2 \times 1 = 2 & 1 \times 6 = 6 & 0 & 0 \\ & 0 & 0 & 2 & 6 \end{array}$$

$\therefore$ mole of AgCl formed = 6

Mass of AgCl formed = $6 \times 143.5 = 861$ g

$[Cr(H_2O)_6](NO_3)_3 = \dfrac{2}{3}$

$\therefore \quad \pi = CST \times (1 + 3\alpha) = \dfrac{2}{3} \times 0.0821 \times 300 \times 4 = 65.68$ atm.

Matching Column Type

17. (a → q, s), (b → q, s), (c → p), (d → s)

(a)

	$K_4[Fe(CN)_6] \rightarrow$	$4K^+ +$	$[Fe(CN)_6]^{-4}$
Initial	1	0	0
After dissociation	$1-\alpha$	4α	α
Total	$1 + 4\alpha > 1$		

(b)

	$Fe_2(SO_4)_3 \rightarrow$	$2Fe^{+3} +$	$3SO_4^{2-}$
Initial	1	0	0
After dissociation	$1-\alpha$	2α	3α
Total	$1 + 4\alpha > 1$		

(c) Glucose does not dissociate

(d)

	$BaCl_2 \rightarrow Ba^{+2}$	+	$2Cl^-$
Initial	1	0	0
After dissociation	$1-\alpha$	α	2α
Total	$1 + 2\alpha > 1$		

Integer Type

18. (2) For isotonic solution, osmotic pressure should be same.

$\therefore \quad \pi_{(NaCl)} = \pi_{(glucose)}$

$iC_1RT = C_2RT$

$iC_1 = C_2$

$$i\frac{(1.17/58.5)}{V} = \frac{7.2/180}{V}$$

$$\Rightarrow \quad i = \frac{7.2 \times 58.5}{1.17 \times 180} = 2$$

19. (3) Given, Normality $= \dfrac{1}{10}$ for $BaCl_2$

$\therefore \quad$ Molarity $= \dfrac{1}{20}$ for $BaCl_2$ $\qquad \left(\because M = \dfrac{N}{\text{Valency}}\right)$

$\because \quad \pi_N = \dfrac{n}{V} \times ST = \dfrac{1}{20} \times 0.0821 \times 300 = 1.2315$ atm

$$\begin{array}{lccc} & BaCl_2 \rightleftharpoons & Ba^{2+} + & 2Cl^- \\ \text{Before dissociation} & 1 & 0 & 0 \\ \text{After dissociation} & (1-\alpha) & \alpha & 2\alpha \end{array}$$

Total mole at equilibrium = $1 + 2\alpha$

and α = 70% or 0.7

Now, $\dfrac{\pi_{\text{exp}}}{\pi_N} = 1 + 2\alpha$

$\therefore \quad \pi_{\text{exp}} = \pi_N \times (1 + 2\alpha) = 1.2315 \times (1 + 2 \times 0.7)$
$= 1.2315 \times 2.7 = 2.955 \approx 3$ atm.

Comprehension Type

20. (b)

	$Ba(NO_3)_2 \rightleftharpoons$	$Ba^{2+} +$	$2NO_3^-$
Initial	1 mole		
After dissoc.	$1-\alpha$	α	2α

Total = $1 + 2\alpha$

$\therefore \quad i = 1 + 2\alpha$

or $\quad \alpha = \dfrac{i-1}{2} = \dfrac{2.74-1}{2} = 0.87 = 87\%$

21. (d) $CaCl_2$ gives maximum particles on dissociation. Hence, ΔT_f is maximum, i.e., T_f is lowest.

CHAPTER 3

DPP 3.1

Subjective Type

1. Alternating current is used in electrolysis so that concentration of ions in the solution remains constant and constant value of resistance is measured.

2. Strong electrolytes dissociated completely even on high concentration. Therefore concentration of such solution is almost same on dilution. Electrolyte 'B' is stronger than 'A' because in 'B' the number of ions remains the same on dilution, but only interionic attraction decreases.

   Therefore Λ_m increases only 1.5 times. While in case of weak electrolyte on dilution, number of constituent ions increases.

3. In the case of CH_3COOH, which is a weak electrolyte, the number of ions increases on dilution due to an increase in degree of dissociation.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

In case of strong electrolyte, the number of ions remains the same but the interionic attraction decreases.

4. Since W = VI, we have

$$I = \frac{100\text{ W}}{110\text{ V}} = \frac{10}{11}\text{A};\ Q = It = \left(\frac{10}{11}\text{A}\right)(10 \times 60 \times 60\text{ s}) = 32727.3\text{ C}$$

Mass Cd deposited

$$(Cd^{2+} + 2e^- \rightarrow Cd) = \frac{M_{Cd}}{2F} \times Q$$

$$= \left(\frac{112.4\text{ g mol}^{-1}}{2 \times 96500\text{ C mol}^{-1}}\right)(32727.3\text{ C})$$

$$= 19.06\text{ g.}$$

5. Let κ_1 and κ_2 be the conductivity of the solutions A and B respectively and the constant of the cell be x.

∴ For solution A:

Conductivity = Conductance × Cell constant

$$\kappa_1 = \frac{1}{50} \times x \qquad (1)$$

For solution B : Conductivity, $\kappa_1 = \frac{1}{50} \times x$ (2)

When equal volumes of A and B are mixed, both the solution get doubly diluted, hence their individual contribution towards the conductivity of the mixture will be $\frac{\kappa_1}{2}$ and $\frac{\kappa_2}{2}$ respectively and the conductivity of the mixture will be $\frac{1}{2}(\kappa_1 + \kappa_2)$.

∴ For the mixture: $\frac{1}{2}(\kappa_1 + \kappa_2) = \frac{1}{R} \times x$ (3)

(R is the resistance of mixture)

From Eqs. (1), (2) and (3),

$R = 66.67$ ohm

6. For 0.001 M CH_3COOH

$$\because \quad \alpha = \frac{\Lambda_{eq.}}{\Lambda^o_{eq.}} \qquad \left(\begin{array}{l}\Lambda_{eq.} = 55\text{ S cm}^2\text{ eq.}^{-1} \\ \Lambda^o_{eq.} = 387\text{ S cm}^2\text{ eq.}^{-1}\end{array}\right)$$

$$\therefore \quad \alpha = \frac{55}{387} = 0.142 \text{ or } 14.2\%$$

Since, $K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.001 \times (0.142)^2}{1 - 0.142}$

$K_a = 2.35 \times 10^{-5}$

∴ Now again $K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.1 \times \alpha^2}{1-\alpha} = 2.35 \times 10^{-5}$

and assume $1 - \alpha = 1$

$$\therefore \quad \alpha_{\text{at }0.1} = 0.015 \text{ or } 1.5\%.$$

7. Suppose water contains N mol/litre or N rq./litre of H⁺ ions or OH⁻ ions.

∵ Eq. of H^+ = Eq. of H_2O

∴ Eq. conductivity of water = Conductivity × $\frac{1000}{N}$

$$= 5.8 \times 10^{-8} \times \frac{1000}{N}$$

Since, water dissociated feebly, i.e., water may be considered to a dilute solution of H^+ and OH^- ions.

$$\therefore \quad \Lambda_{eq.\,H_2O} = \Lambda^o_{eq.\,H_2O} = \lambda^o_{H^+} + \lambda^o_{OH^-}$$

$$\therefore \quad 5.8 \times 10^{-8} \times \frac{1000}{N} = 350 + 198 = 548$$

$$\therefore \quad N = 1.058 \times 10^{-7}$$

$$\therefore \quad [H^+] = [OH^-] = 1.058 \times 10^{-7}$$

For the equilibrium, $H_2O \rightleftharpoons H^+ + OH^-$

$$\text{Equilibrium constant (K)} = \frac{[H^+][OH^-]}{[H_2O]}$$

$$\text{or} \quad K_w = K \times [H_2O] = [H^+][OH^-]$$

$$= 1.058 \times 10^{-7} \times 1.058 \times 10^{-7} = 1.119 \times 10^{-14}$$

$$\therefore \quad K = \frac{K_w}{[H_2O]} = \frac{1.119 \times 10^{-14}}{55.5} = 2 \times 10^{-16}\text{ mol/litre}$$

$$\left[[H_2O] = \frac{1000}{18} = 55.5\text{ mol/litre}\right].$$

Single Correct Answer Type

8. **(b)** $K = \kappa R = (6.67 \times 10^{-3}\ \Omega^{-1}\text{ cm}^{-1})(243\ \Omega) = 1.62\text{ cm}^{-1}$.

9. **(b)** We have

$$\underset{c(1-\alpha)}{CH_3COOH} \rightleftharpoons \underset{C\alpha}{CH_3COO^-} + \underset{c\alpha}{H^+}$$

$$K = \frac{[CH_3COO][H^+]}{[CH_3COOH]} = \frac{c\alpha^2}{(1-\alpha)}$$

Since, $\alpha = \Lambda_c/\Lambda^\infty$, we get $K = \dfrac{c(\Lambda_c/\Lambda^\infty)^2}{1-(\Lambda_c/\Lambda_\infty)} = \dfrac{c\Lambda_c^2}{\Lambda^\infty(\Lambda^\infty - \Lambda_c)}$

10. (c) $\kappa = \Lambda c = (200 \text{ S cm}^2 \text{ mol}^{-1})(0.05 \times 10^{-3} \text{ mol cm}^{-1})$

$= 0.01 \text{ S cm}^{-1}$

$$R = \frac{1}{\kappa}\left(\frac{\ell}{A}\right) = \frac{1}{(0.01 \text{ S cm}^{-1})}\left(\frac{1}{3}\text{cm}^{-1}\right) = 33.33\ \Omega.$$

11. (a) $\Lambda_m^\infty(\text{potash alum}) = 2\Lambda_m^\infty(K^+) + 2\Lambda_m^\infty(\text{Al}^{3+}) + 4\Lambda_m^\infty(\text{SO}_4^{2-})$

$= (2 \times 73.5 + 2 \times 189 + 4 \times 160) \text{ S cm}^2 \text{ mol}^{-1}$

$= 1165 \text{ S cm}^2 \text{ mol}^{-1}$.

12. (c) For a weak electrolyte, Λ_m increases sharply near high dilution. Hence, an extrapolation at infinite dilution is not possible.

13. (a). Resistance = specific resistance × cell constant

$$(\text{R})_{\text{KCl}} = (\text{S})_{\text{KCl}} \times (\text{cell constant})$$

$$(\text{R})_{\text{NaOH}} = (\text{S})_{\text{NaOH}} \times (\text{cell constant})$$

$$\frac{(\text{R})_{\text{KCl}}}{(\text{R})_{\text{NaOH}}} = \frac{(\text{S})_{\text{KCl}}}{(\text{S})_{\text{NaOH}}}$$

$$\frac{160}{190} = \frac{700}{(\text{S})_{\text{NaOH}}}$$

$\therefore \quad (\text{S})_{\text{NaOH}} = 831.25$ ohm-cm

$\therefore$ specific conductance $(\kappa) = 1.20 \times 10^{-3}\ \Omega^{-1} \text{ cm}^{-1}$.

14. (c) We know that the electrical resistance of electrolytic solutions is directly proportional to its length (l) and inversely proportional to its area of cross-section (a) i.e.,

$$R \propto \frac{1}{a} \Rightarrow R = \rho\frac{1}{a}$$

Comparing with $y = mx + c$.
The graph of R vs ($1/a$) will be a straight line starting from the origin with slope ρ.

15. (a) $\Lambda_v = \dfrac{\kappa \times 1000}{M} = \dfrac{0.158 \times 1000}{0.02} = 7900 \text{ S cm}^2 \text{ mol}^{-1}$

Also, $\alpha = \dfrac{\Lambda_v}{\Lambda_\infty} = \dfrac{7900}{10^5} = 0.079$

$\therefore \quad [\text{Li}^+] = c\alpha = 0.02 \times 0.079 = 1.58 \times 10^{-3}$

$\therefore \quad w_{\text{Li}^+} = 1.58 \times 10^{-3} \times 7 = 0.01106$ g/litre

16. (a) $\lambda^\circ_{\text{Ag}^+} = 5.7 \times 10^{-4} \times 96500 \quad (\lambda^\circ = u^\circ \times F)$

$\lambda^\circ_{\text{NO}_3^-} = 6.9 \times 10^{-4} \times 96500$

$\therefore \quad \Lambda^\circ_{\text{M AgNO}_3} = \lambda^\circ_{\text{Ag}^+} + \lambda^\circ_{\text{NO}_3^-}$

$= (5.7 \times 10^{-4} + 6.9 \times 10^{-4}) \times 96500$

$= 121.59 \text{ S cm}^2 \text{ mol}^{-1}$

17. (d) Initial conductance (Λ) of solution was due to K^+_{aq} and Cl^-_{aq}. On addition of $\text{AgNO}_{3\,(\text{aq.})}$, the reaction occurs

$$\text{AgNO}_3(\text{aq}) + \text{KCl}(\text{aq}) \rightarrow \text{AgCl} + \text{KNO}_3(\text{aq})$$

$\Lambda_{\text{KCl}} = \Lambda_{\text{KNO}_3}$ till complete precipitation and then increases with further addition of AgNO_3.

Multiple Correct Answers Type

18. (a, b, c, d)

(a) $\text{C}_\text{T} = \Sigma\text{C}_\text{i} + \text{C}_{\text{water}}$

(b) Due to more hydration of small cation and thus size increases and conductance decreases.

(c) Due to Grothus conductance, conductance of NH_4^+ in NH_3 is more.

19. (a, b)

Speed $= \dfrac{0.4}{60} = 6.67 \times 10^{-3} \text{ cm sec}^{-1} = 6.67 \times 10^{-5} \text{ m sec}^{-1}$

Ionic mobility $= \dfrac{\text{Speed}}{\text{Pot. gradient}} = \dfrac{6.67 \times 10^{-5} \times 3 \times 10^{-2}}{2}$

$= 1 \times 10^{-6} \text{ m}^2 \text{ volt}^{-1} \text{ sec}^{-1}$.

20. (a, c)

$\text{H}^\oplus$ has $\Lambda_m^{oo} = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\text{OH}^\ominus$ has $199.1 \text{ S cm}^2 \text{ mol}^{-1}$.

21. (b, c)

Degree of dissociation is calculated for weak electrolytes.

22. (a, b, c, d)

All these factors affect the conductance of solution.

23. (a, c, d)

On dilution the molar conductance of the electrolyte solution will increase exponentially.

24. (a, b, d)

Linear plot corresponds to strong electrolyte while the exponential curve corresponds to weak electrolyte.

Matching Column Type

25. (a → s), (b → u), (c → t), (d → p), (e → q), (f → r)

Conductance $= \dfrac{1}{\text{Resistance}} = \dfrac{1}{\text{ohm}} = \text{ohm}^{-1} = \text{siemen}$

Resistivity $= \rho = R \times \dfrac{a}{\ell} = \text{ohm} \times \dfrac{\text{m}^2}{\text{m}} = \text{ohm m}$

Conductivity $= \dfrac{1}{\rho} = \text{ohm}^{-1}\text{ m}^{-1} = \text{siemen m}^{-1}$

Molar conductivity $= \Lambda_m = \kappa_c \times \dfrac{1000}{\text{Molarity}} = \text{ohm}^{-1}\text{ m}^{-1} \times \dfrac{\text{m}^3}{\text{mol}}$

$= \text{S m}^2 \text{ mol}^{-1}$

Cell constant $= \dfrac{\ell}{a} = \dfrac{\text{m}}{\text{m}^2} = \text{m}^{-1}$

Resistance $= \dfrac{V}{I} = \text{volt ampere}^{-1}$

Integer Type

26. (4) $\alpha = \dfrac{\Lambda_m^c}{\Lambda_m^o} = \dfrac{3.907}{390.7} = 0.01$

	$\text{CH}_3\text{COO} \rightleftharpoons$	$\text{CH}_3\text{COO}^\ominus$	+	$\text{H}^\oplus$
Initial conc.	c	0		0
Final conc.	$c(1 + \alpha)$	$c\alpha$		$c\alpha$

$\therefore \quad [\text{H}^\oplus] = c\alpha = 0.01 \times 0.01 = 10^{-4}$ M

$\text{pH} = -\log(10^{-4}) = 4$.

27. (5)

$$R = \rho \times \frac{\ell}{a}$$

$$\frac{\ell}{a} = R \times \frac{1}{\rho} = R \times k$$

$$= 2000 \times 0.002501 = 5.002 \cong 5$$

Comprehension Type

8. (c) $\pi_m = \pi_m^{\infty} - b\sqrt{c}$; $c = 4 \times 10^{-4}(M)\pi_m = 107$

or $107 = \pi_m^{\infty} - b \times 2 \times 10^{-2}$ (1)

$97 = \pi_m^{\infty} - b \times 3 \times 10^{-2}$ (2)

or $10 = b \times 10^{-2}$ or $b = 1000$ and $\pi_m^{\infty} = \pi_m + b\sqrt{c}$

or $\pi_m^{\infty} = 107 + 10^3 \times 2 \times 10^{-2}$

or $\pi_m^{\infty} = 127\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

(d) For $25 \times 10^{-4}(M)$ NaCl, $\pi_m = \pi_m^{\infty} - b\sqrt{c}$

or $\pi_m = 127 - 10^3 \times (25 \times 10^{-4})^{1/2}$

or $\pi_m = 127 - 10^3 \times 5 \times 10^{-2} = 127 - 50$

or $\pi_m = 77\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

$$R = \rho \times \frac{\ell}{A}$$

or $\frac{1}{R} = R \times \frac{A}{\ell} = \frac{\kappa}{K_c}$ where K_C is the cell constant.

or $K_C = \kappa \times R$

$$\pi_m = \frac{10^3 \times \kappa}{C}$$

or $77 = \frac{10^3 \times \kappa}{25 \times 10^{-4}}$

or $\kappa = 77 \times 25 \times 10^{-7}\ \text{ohm}^{-1}\ \text{cm}^{-1}$

$\therefore$ $K_C = 77 \times 25 \times 10^{-7} \times 10^3 = 77 \times 25 \times 10^{-4} = 0.1925\ \text{cm}^{-1}$

0. (d) For Na_2SO_4 solution, $\kappa = \frac{K_C}{R} = \frac{0.1925}{400}$

$$= 4.81 \times 10^{-4}\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

$\therefore$ $\pi_m(Na_2SO_4) = \frac{10^3 \times \kappa}{C} = \frac{10^3 \times 4.81 \times 10^{-4}}{\frac{5}{2} \times 10^{-3}}$

or $\pi_m(Na_2SO_4) = \frac{2}{5} \times 4.81 \times 100\ \text{ohm}^{1}\ \text{cm}^2\ \text{mol}^{-1}$

or $\pi_m(Na_2SO_4) = 192.4\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

DPP 3.2

Subjective Type

1. In case of platinum electrodes, the products are Cu on cathode and O_2 gas on anode. This is because out of Cu^{2+} and H^+ ions (produced from H_2O), Cu^{2+} ions have lower discharge potential. Out of SO_4^{2-} and OH^- ions, OH^- ions have lower discharge potential ($\bar{OH} \rightarrow OH + e^-$, $4OH \rightarrow 2H_2O + O_2$)

In case of copper electrodes, product at cathode is the same, *viz.*, Cu but at anode, out of the three possible reactions, *viz.*,

$$OH^- \rightarrow OH + e^-,\ SO_4^{2-} \rightarrow SO_4 + 2e^-,$$

$$Cu \rightarrow Cu^{2+} + 2e^-,$$

Cu is more easily oxidized than OH^- and SO_4^{2-} ions. Hence, anode of Cu dissolves into the solution to form Cu^{2+} ions.

2. (i) $H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$

$H_2O \rightleftharpoons H^+ + OH^-$

At cathode: $H^+ + e \rightarrow H$, $H + H \rightarrow H_2(g)$

At Anode: $OH^- \rightarrow OH + e^-$, $4OH \rightarrow 2H_2O(\ell) + O_2(g)$

Thus, H_2 is liberated at the cathode and O_2 at the anode.

(ii) $AgNO_3(s) + aq \rightarrow Ag^+(aq) + NO_3^-(aq)$

$H_2O \rightleftharpoons H^+ + OH^-$

At cathode: Ag^+ ions have lower discharge potential than H^+ ions. Hence, Ag^+ ions will be deposited on the cathode ($Ag^+ + e^- \rightarrow Ag$).

At anode: Ag anode will be attacked by NO_3^- ions. Hence, Ag anode will dissolve forming Ag^+ ions in the solution ($Ag \rightarrow Ag^+ + e^-$).

3. The changes taking place at the electrodes in the electrolysis of $Ni(NO_3)_2$ solution using nickel electrodes will be as follows:
At cathode: $Ni^{2+} + 2e^- \rightarrow Ni$
At anode: $Ni \rightarrow Ni^{2+} + 2e^-$
Thus, amount of nickel deposited on the cathode from the solution = nickel dissolved from the anode.
Hence, molarity of the solution will remain unchanged at the end of the electrolysis.

4. (i) This is because H^+ ions produced from ionization of water have lower discharge potential than Na^+ ions produced from ionization of NaCl or reduction potential of water is greater than that of sodium ions.

(ii) The reactions at cathode for the deposit of Na and Al are $Na^+ + e^- \rightarrow Na$ and $Al^{3+} + e^- \rightarrow Al$

Thus, 1 faraday deposits 1 mol of Na whereas 3 faradays are required for depositing one mol of Al.

Single Correct Answer Type

5. (d) The reactions are

$$2H^+ + 2e^- \rightarrow H_2 \text{ and } 2H_2O \rightarrow 4H^+ + O_2 + 4e^-$$

The volume of H_2 liberated will be twice that of O_2.

6. (b) Using the expression $m = \frac{It}{F}\frac{M}{|v_e|}$

We get $m = \frac{(8.46\ \text{A})(8 \times 60 \times 60\ \text{s})(107.8\ \text{g mol}^{-1})}{(96500\ \text{C mol}^{-1})(1)} = 272.18\ \text{g}$

Volume of silver plated out, $V = \frac{m}{\rho} = \frac{272.18\ \text{g}}{10.5\ \text{g cm}^{-3}} = 25.92\ \text{cm}^3$

Area of the tray plated $= \frac{25.92\ \text{cm}^3}{0.00254\ \text{cm}} = 10204.7\ \text{cm}^2$

7. (c) $Ag^+ + e^- \rightarrow Ag$ $\frac{0.54}{108} = 5 \times 10^{-3}$ mol

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

$n_{H_2} = 2.5 \times 10^{-3}$, $V_{H_2} = \frac{2.5 \times 10^{-3} \times 24.63}{728/760} = 64.28$ mL

8. (b) The reactions are $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ and $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
For the passage of 4 mol of electrons, the net reaction occurring is

$$6H_2O \rightarrow O_2 + 2H_2 + 4H^+ + 4OH^- \text{ or } 2H_2O \rightarrow 2H_2 + O_2$$

that is, 2 mol of water (i.e. 36 g) is deposited by the passage of 4 mol of electrons. Thus

$$\text{Time required to decompose water} = \frac{4 \text{ mol electrons}}{36 \text{ g } H_2O}$$

$$= (18 \text{ g } H_2O)\,(96500 \text{ C}/2\text{A}) = 96500 \text{ s} \equiv 26.8 \text{ h}$$

9. (a) 1 F = Charge on 1 mole of e^- s

Let charge on one $e^- = x$

Then charge on 1 mol of e^-s $= x \times N_A$

$\Rightarrow \quad 1 \text{ F} = x \times N_A$

$\Rightarrow \quad x = \dfrac{1 \text{ F}}{N_A}$

10. (c) Since anode is copper, the reaction occurring here is $Cu \rightarrow Cu^{2+} + 2e^-$. Thus, there will occur a loss of Cu at anode which will also equal to 3.15 g.

11. (c) $Na^+ \; + \; e^- \; \rightarrow \; Na(s)$

1 mole 1 faraday

$Al^{3+} + 3e^- \rightarrow Al(s)$

1 faraday

No. of mole of Al = $\dfrac{1}{3}$ mole.

Multiple Correct Answers Type

12. (a, d)

In aqueous solution, it is H_2O which is reduced.

$$2H_2O + 2e^- \rightarrow 2H_2 + 2OH^-.$$

The impure metal is made anode and undergoes oxidation.

13. (b, c, d)

SO_2^- is difficult to oxidize and water is oxidized instead.

Larger the reduction potential, larger the tendency for reduction.

14. (c, d)

It is oxygen liberated instead of F_2.

Pure metal is made cathode where metallic ions in solution get reduced to pure metal.

15. (b, d)

	Ag		Cu		Au
Equivalent ratio	1	:	1	:	1
Mole ratio	$\frac{1}{1}$	:	$\frac{1}{2}$	:	$\frac{1}{3}$
	6	:	3	:	2

16. (a, b, d)

(a) Anode $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

(b) Anode $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

(c) Anode $Cu \rightarrow Cu^{2+} + 2e^-$

(d) Anode $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Matching Column Type

17. (a → p), (b → q), (c → r), (d → s)

(a → p)

$$2 \text{ F} = 2 \text{ Eq of } \overset{\ominus}{O}H$$

$$[\overset{\ominus}{O}H] = \frac{2\text{Eq}}{100 \text{ L}} = 2 \times 10^{-2} \text{ N}$$

$$pOH = 1.7,\ pH = 14 - 1.7 = 12.3$$

At anode: Ethane(g) + CO_2(g)

At cathode: H_2(g)

(b → q)

$$1 \text{ F} = 1 \text{ Eq of } \overset{\ominus}{O}H$$

$$[\overset{\ominus}{O}H] = \frac{1 \text{ Eq}}{10 \text{ L}} = 10^{-1} \text{ N}$$

$$pOH = 1,\ pH = 14 - 1 = 13$$

At anode: H_2(g) + CO_2(g)

At cathode: H_2(g)

(c → r)

$$1 \text{ F} = 1 \text{ Eq } \overset{\ominus}{O}H = 1 \text{ Eq } H^{\oplus}$$

So solution is neutral.

$\therefore \quad pH = 7$

At anode: O_2(g)

At cathode: H_2(g)

(d → s)

$$CuF_2 \xrightarrow{\text{Electrolysis}} Cu^{2+} + 2F^{\ominus}$$

At cathode: $Cu^{2+} + 2e^- \rightarrow Cu(s)$

At anode: $H_2O \rightarrow \frac{1}{2}O_2(g) + 2H^{\oplus} + 2e^-$

(Since $E^{\ominus}_{\text{oxid of } H_2O} > E^{\ominus}_{\text{oxid of } F^{\ominus}}$)

At anode:

$$1 \text{ F} = 1 \text{ Eq } H^{\oplus};\ [H^{\oplus}] = \frac{\text{Eq}}{V_L} = \frac{1 \text{ Eq}}{10 \text{ L}} = 10^{-1} \text{ N}$$

pH = 1.

Integer Type

18. (3) Molten NaCl $\xrightarrow{\text{Electrolysis}} Na^{\oplus} + Cl^{\ominus}$

Number of Faradays

$$= \frac{I \times t \text{ in seconds}}{96500 \text{ C}} = \frac{5.5 \text{ s} \times 25 \times 60 \text{ s}}{96500 \text{ C}} = 0.085 \text{ F}$$

$$1 \text{ F} = 1 \text{ equivalent of } Cl_2 = \frac{71 \text{ g}}{\text{Charge}} = \frac{71}{2}\text{g}$$

$$\therefore \quad 0.085 \text{ F} = \frac{71}{2} \times 0.085 = 3.017 \text{ g } Cl_2.$$

19. (2)

Aqueous solution of $CuSO_4$ on elecrolysis gives Cu at cathode and O_2 at anode and H^+ ions in the solution.

$$\text{Eq of current} = \frac{96.5 \text{ A} \times 10 \text{ s}}{96500 \text{ C}} = 0.01 \text{ Eq} = 10^{-2} \text{ Eq}$$

$$\therefore \quad 10^{-2} \text{ Eq of Cu} = 10^{-2} \text{ Eq of } O_2 \equiv 10^{-2} \text{ of } H^{\oplus} \equiv 10^{-2} \text{ F.}$$

$$\therefore \quad [H^{\oplus}] = \frac{10^{-2} \text{ Eq.}}{\text{Volume of solution in L}} = \frac{10^{-2} \text{ Eq}}{1 \text{ L}} = 10^{-2} \text{ N or M}$$

$$\therefore \ pH = -\log(10^{-2}) = 2.$$

Comprehension Type

20. (d) $CuSO_4(aq) \rightarrow Cu^{2+} + SO_4^{2-} + H^+ + OH^-$

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu(s)$

Anode: $2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

Remaining solution will contain H_2SO_4.

21. (b) $NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H^+ + OH^-$

Cathode: $2H^+ + 2e^- \rightarrow H_2$

Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

22. (b) Anodic process will be:

$$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$$

23. (c) $BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$

1 mol BeO_3^- requires 6 mol e^-, i.e., 6 faraday charge.

24. (b) Anodic process: $2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

$$V = \frac{It\,V_e}{96500}$$

$$= \frac{1 \times 965 \times 5.6}{96500} = 0.056 \text{ L}$$

$$= 56 \text{ mL at S.T.P.}$$

DPP 3.3

Subjective Type

1. (i) Fuel cell is environmental friendly cell. It does not require recharging like those of secondary cells. Future generation vehicles will be driven by fuel cells.

   (ii) Discharging process of lead storage battery is:

   $$Pb(s) + PbO_2(s) + 2H_2SO_4(aq.) \rightarrow 2PbSO_4(s) + 2H_2O(\ell)$$

   Sulphuric acid is used as electrolyte in this cell. When cell is discharged, the density of electrolyte solution decreases because H_2SO_4 is consumed while water is produced.

2. (i) $ZnCl_2$ combines with NH_3 produced to form the complex salt $[Zn(NH_3)_2Cl_2]$ as otherwise the pressure developed due to NH_3 would crack the seal of the cell.

   (ii) This is because the electrolyte KOH is not consumed in the reaction.

3. Those cells are rechargeable in which the products formed during discharge are deposited on the electrodes and these can be decomposed to give the original substances when electrical energy is supplied.

4. Weight of solution before discharge = 3500 × 1.294 = 4529 g

   Weight of H_2SO_4 before discharge = $\frac{39}{100} \times 4529 = 1766.31$ g

   Weight of solution after discharge = 3500 × 1.139 = 3986.5 g

   Weight of H_2SO_4 after discharge = $\frac{20}{100} \times 3986.5 = 797.3$ g

   Loss in mass of H_2SO_4 during discharge = 1766.31 − 797.3
   = 969.01 g

   Now from first law of electrolysis,

   $$W = \frac{Q \times E}{96500}$$

   $$969.01 = \frac{Q \times 98}{96500} \Rightarrow Q = 954178.21 \text{ coulomb}$$

   $$\text{Ampere} - \text{hour} = \frac{\text{Coulomb}}{3600} = \frac{954178.21}{3600}$$

   $$= 265.04 \text{ ampere-hour}$$

5. Reaction at anode of fuel cell,

   $$\underset{\substack{\text{1 mole}\\ 22.4\text{ L}}}{H_2(g)} \rightarrow 2H^+ + \underset{\substack{\text{2 mole}\\ 2\text{ F}}}{2e^-}$$

   67.2 L of H_2 correspond $= \frac{2 \times 96500}{22.4} \times 67.2$ coulomb

   Time = 15 × 60 seconds

   Average current $= \frac{2 \times 96500 \times 67.2}{22.4 \times 15 \times 60} = 643.3$ amp

   Mass of copper deposited by $\frac{2 \times 96500}{22.4} \times 67.2$ coulomb

   $$= \frac{63.5}{2 \times 96500} \times \frac{2 \times 96500 \times 67.2}{22.4} = 190.5 \text{ g}$$

Single Correct Answer Type

6. (d) The reactions occurring operation of battery are

   Anode: $Pb(s) + HSO_4^- + H_2O\ PbSO_4(s) + 2e + H_3O^+$; $E^\circ_{OP} = +0.356$ V

   Cathode: $PbO_2 + HSO_4^- + 3H_3O^+ + 2e \rightarrow PbSO_4(s) + 5H_2O$; $E^\circ_{RP} = +1.685$ V

   Net change: $Pb(s) + 2HSO_4^- + 2H_3O^+ + PbO_2(s) \rightarrow 2PbSO_4(s) + 4H_2O$; $E^\circ = 2.041$ V

7. (b) MnO_2 in Lechlanche cell.
8. (b) $H_2 - O_2$ cell
9. (a) $Pb^{2+} + 2e^- \rightarrow Pb$
10. (a) An important application of fuel cell used in space programmes to provide power for heat and light as well as drinking water to astronauts.
11. (b) Fuel cell involves direct conversion of chemical energy into electrical energy.

    At anode: $2H_2(g) + 4OH^- \rightarrow 4H_2O(\ell) + 4e$

    At cathode: $O_2 + 2H_2O(\ell) + 4e \rightarrow 4OH^-(aq)$

    $$H_2 + \frac{1}{2}O_2 \rightarrow H_2O(\ell)$$

    $E = +ve$.

Multiple Correct Answers Type

12. (a, b, c)

    All of these are characteristics of fuel cells.

13. (a, b, c, d)

    All are correct regarding lead storage batteries.

14. (a, b, c)

    The potential of each Ni–Cd cell is 1.4 V.

15. (a, c, d)

The charging of lead storage battery involves the reverse reactions.

$$PbSO_4 + H_2O \rightarrow PbO_2 + SO_4^{2-} + 2H^+$$

16. (a, c)
In $H_2 - O_2$ fuel cell, hydrogen and oxygen gases are bubbled through the porous electrodes into the KOH/NaOH solution. The following electrode reactions takes place

$O_2(g) + 2H_2O(\ell) + 4e^- \rightarrow 4OH^-(aq.)$ (at cathode)

$2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(\ell) + 4e^-$ (at anode)

Overall: $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$

Matching Column Type

17. (a → s), (b → r), (c → p), (d → q)

Lechlanche cell: A dry cell is a compact form of the Leclanche cell. It consists of a cylindrical zinc container which acts as the anode.

$Zn \rightarrow Zn^{2+} + 2e^-$

Ni-Cd cell: It is a rechargeable cell which is becoming more and more popular especially in the calculators. It consists of a cadmium electrode (as anode) and a metal grid containing nickel (IV) oxide (as cathode) immersed in KOH solutions.

Fuel cell:

At anode: $2H_2(g) + 4\overset{\ominus}{O}H(aq) \rightarrow 4H_2O(l) + 4e^-$

At cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4\overset{\ominus}{O}H(aq)$

Overall reaction: $2H_2O(g) + O_2(g) \rightarrow 2H_2O(l)$

Mercury cell: It consists of zinc container as the anode, a carbon rod as the cathode, and moist mercuric oxide mixed with KOH as the electrolyte filled between the two electrons.

Integer Type

18. (2 V). The emf of lead storage battery is 2 V and thus, a lead accumulator of six plates produces an emf of 12 V and of twelve plates 24 V.

Comprehension Type

19. (d) At anode, oxidation occurs. $PbSO_4$ is oxidized to PbO_2 according to reaction (d).

20. (a) Mass of the solution before discharge

$= 3500 \text{ mL} \times 1.294 \text{ g mL}^{-1} = 4529 \text{ g}$

Mass of H_2SO_4 present in this solution

$= \dfrac{39}{100} \times 4529 \text{ g} = 1766.31 \text{ g}$

Mass of the solution after discharge

$= 3500 \text{ mL} \times 1.139 \text{ g mL}^{-1} = 3986.5 \text{ g}$

Mass of H_2SO_4 present in this solution

$= \dfrac{20}{100} \times 3986.5 \text{ g} = 797.3 \text{ g}$

Loss in mass of H_2SO_4 during discharge

$= 1766.31 - 797.3 = 969.01 \text{ g}$

Moles of H_2SO_4 lost during discharge $= \dfrac{969.01}{98} = 9.88786$

21. (c) Moles of H_2SO_4 present in the solution after discharge

$= \dfrac{797.3}{98} = 8.136$

$\therefore$ Molarity of the solution $= \dfrac{8.136 \text{ moles}}{3.5 \text{ L}} = 2.32.$

22. (a) During the discharge reaction, 4 moles of H^+ ions, i.e., 2 moles of H_2SO_4 require 2 F, i.e., 2×96500 coulombs

$\therefore$ 9.88786 moles will require $= \dfrac{2 \times 96500 \times 9.88786}{2}$

$= 954178$ coulombs

23. (b) Ampere-hour $= \dfrac{\text{Coulombs}}{3600 \text{ s}} = \dfrac{954178}{3600} = 265.05$

DPP 3.4

Subjective Type

1. (a) To predict reaction of zinc with sulphuric acid: If it reacts, the following reaction should take place:

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$, i.e., $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

By convention, the cell will be represented as: $Zn|Zn^{2+}||H^+|H_2$

Std. EMF of the cell

$$(E^o_{cell}) = \begin{bmatrix}\text{Std. redn. pot. of} \\ \text{R.H.S. electrode}\end{bmatrix} - \begin{bmatrix}\text{Std. redn. pot. of} \\ \text{L.H.S. electrode}\end{bmatrix}$$

$= 0 - (-0.76) = +0.76$ volt.

Thus, the EMF of the cell comes out to be positive. Hence, the reaction takes place.

(b) To predict the reaction of silver with sulphuric acid : If it reacts, the following should take place.

$2Ag + H_2SO_4 \rightarrow Ag_2SO_4 + H_2$, i.e., $2Ag + 2H^+ \rightarrow 2Ag^+ + H_2$

By convention, the cell may be represented as: $Ag|Ag^+||H^+|H_2$

$$E^o_{cell} = E^o_{H^+,H_2} - E^o_{Ag^+,Ag} = 0 - 0.80 = -0.80 \text{ volt.}$$

Thus, EMF of the supposed cell comes out to be negative. This reaction does not take place.

2. The reaction can be either $Br_2 + 2I^- \rightarrow 2Br^- + I_2$ or $I_2 + 2Br^- \rightarrow 2I^- + Br_2$

For 1st reaction, E.M.F. $= E^o_{Br_2/Br^-} - E^o_{I_2/I^-} = 1.08 - 0.54$
$= 0.54$ V

For 2nd reaction, E.M.F. $= -E^o_{I_2/I^-} - E^o_{Br_2/Br^-} = 0.54 - 1.08$
$= -0.54$ V

As E.M.F. is positive for the 1st reaction, hence the cell reaction is

$$Br_2 + 1I^- \rightarrow 2Br^- + I_2.$$

3. (i) CuO; CuO is below hydrogen in series, so it can reduce from CuO to Cu.

(ii) Ag_2O; Lower in series, stability of oxide become lesser.

(iii) Lower SRP metal can displace higher SRP metals ions from solution.

4. (a) $0.34 < E^o < 0.8$,

Metal should be below hydrogen and Cu^{2+} but should be above Ag^+ in series.

(b) $-0.44 < E^o < 0$

Metal should be above hydrogen but should be below Zn^{2+} and Fe^{2+} both.

Single Correct Answer Type

(a) More negative the standard potential, least the reduction tendency of the ion. The corresponding atom has largest oxidation tendency and thus is a strong reducing agent. In the present case, Zn is the strongest reducing agent.

(a) From the first reaction, we conclude $E^{o}_{Y^-/Y_2} > E^{o}_{X^-/X_2}$

From the second reaction, we conclude $E^{o}_{W^-/W_2} > E^{o}_{Y^-/Y_2}$

From the third reaction, we conclude $E^{o}_{X^-/X_2} > E^{o}_{Z^-/Z_2}$

Hence, $E^{o}_{W^-/W_2} > E^{o}_{Y^-/Y_2} > E^{o}_{X^-/X_2} > E^{o}_{Z^-/Z_2}$.

7. (a) The reduction tendencies is Z > Y > X. Hence, Y can oxidise X and not Z.

8. (d) Since $E^{o}(Fe^{3+}, Fe^{2+}/Pt)$, $E^{o}(Cu^{2+}/Cu)$ and $E^{o}(Ag^{+}/Ag)$ are greater than $E^{o}(Co^{2+}/Co)$, Co metal will be able to reduce Fe^{3+} to Fe^{2+}, Cu^{2+} to Cu and Ag^{+} to Ag.

9. (b) Larger the reduction potential, larger the oxidation tendency of the ion being reduced. Hence, the oxidizing tendency follows the order $Pb^{4+} > Hg^{2+} > Sn^{4+}$.

Lesser the reduction potential, larger the reduction tendency of the ion formed in the reduction reaction. Hence, the reducing tendency follows the order $Sn^{2+} > Hg^{2+} > Pb^{2+}$.

10. (c) The cell reaction giving E^{o}_{cell} positive is

$$Hg_2^{2+} + Sn \rightarrow 2Hg + Sn^{2+} \cdot E^{o}_{cell} = E^{o}_{Hg_2^{2+}/Hg} - E^{o}_{Sn^{2+}/Sn}$$

From this, it follows that Hg_2^{2+} can oxidize Sn to Sn^{2+}.

11. (b) More positive potential mean more easily ion is reducible and more difficult is the oxidation of the corresponding atom. Reducing power of the metal means more easily the metal should be oxidizable.

12. (d) The electrode, which shows colour change during redox process is called indicator electrode.

13. (a) pH of solution due to formation of LiOH or due to increase in $[OH^-]$ because H^+ ions are discharged at cathode in preference to Li^+.

14. (d) $AgNO_3 + KCl \rightarrow AgCl \downarrow + KNO_3$.

Multiple Correct Answers Type

15. (a, b, c, d)

All of the above statements are characteristics of standard hydrogen electrode.

16. (a, c)

The functioning of glass electrode depends on the potential difference across the glass membrane separating solutions of different pH. The electrode potential of glass electrode depends only on $[H^+]$.

17. (a, d)

The standard reduction potential of Cl_2 is more than that of I_2. The product formed when I_2 combines with starch is blue in colour.

18. (a, c)

The standard reduction potential of copper metal is higher than Zn^{+2}. So, Cu metal can't be oxidized by Zn^{+2} ions.

19. (a, b, c)

In these three reactions salt bridge is not necessary because the reactants are not soluble. For example, Pb and PbO_2 are not soluble. They are made into plates and immersed in H_2SO_4 solution. The plates are not in physical contact. Both the reactants turn into $PbSO_4$ which is also insoluble and stays on/in the plates so that the cell can be easily recharged by a reverse current.

Matching Column Type

20. (a → r), (b → p), (c → v), (d → t), (e → s), (f → q), (g → v, u)

Half Cell	Reduction potentials (V)
$Li^{\oplus}/Li$	–3.04
Pt, $Br_2/Br^{\ominus}$	1.09
Au^{3+}/Au	1.40
Pt, $F_2/F^{\ominus}$	2.87

If the standard reduction potential of an electrode is greater than zero, then its reduced form is more stable compared to H_2 gas. In other words, the substance element or ion is more easily reduced and is a stronger oxidizing agent. Similarly, if the standard electrode potential is negative, then H_2 gas is more stable than the form of the species. In other words, the substance (element or ion) is less easily reduced and is a weaker oxidizing agent.

Integer Type

21. (3)

$$Fe \rightarrow Fe^{2+} + 2e^-; \quad E_1^o \qquad (1)$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^-; \quad E_2^o \qquad (2)$$

Adding (1) and (2)

$$Fe \rightarrow Fe^{3+} + 3e^-; \quad E_3^o \qquad (3)$$

$$\Delta G_1^o = -2\,FE_1^o$$

$$\Delta G_2^o = -1\,FE_2^o$$

$$\Delta G_3^o = \Delta G_1^o + \Delta G_2^o$$

$$-3FE_3^o = -2FE_1^o - 1FE_2^o$$

$$\therefore \quad E_3^o = \frac{E_2^o + 2E_1^o}{3}$$

22. (3)

$$Fe \rightarrow Fe^{2+} + 2e^-; \quad E_1^o \qquad (1)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+}; \quad E_2^o \qquad (2)$$

Adding Eq. (1) and 2 × Eq. (2)

$$Fe + 2Fe^{3+} \longrightarrow 3Fe^{2+}; \quad E_3^o$$

∴ 3 cells can be constructed with different E^{o}_{Cell}.

Comprehension Type

23. (d)

$$Cu^{2+} + e \rightarrow Cu^{+}; \quad -\Delta G_1^o = E_1^o\,F \times 1$$

$$Cu^{+} + e \rightarrow Cu; \quad -\Delta G_2^o = E_2^o\,F \times 1$$

$$Cu^{+} + e \rightarrow Cu; \quad -\Delta G_3^o = -[-\Delta G_1^o - -\Delta G_2^o]$$

$$= -[0.15\,F + 0.5\,F]$$

$$\text{or} \quad 2 \times E_3^o\,F = 0.65\,F$$

$$\therefore \quad E_3^o = 0.325\,V$$

$\therefore \quad Cu \rightarrow Cu^{2+} + 2e; \qquad E^o = -0.325$ V

24. (b) $Cu \rightarrow Cu^{2+} + 2e$

$2Ag^+ + 2e \rightarrow 2Ag$

$$\therefore \quad E^o_{cell} = E^o_{OP_{Cu/Cu^{2+}}} + E^o_{RP_{Ag^+/Ag}}$$

$$= -0.325 + 0.799 = 0.474 \text{ V}$$

25. (a) $$E_{cell} = E^o_{cell} + \frac{0.059}{2}\log\frac{[Ag^+]^2}{[Cu^{2+}]}$$

$$= +0.474 + \frac{0.059}{2}\log\frac{(0.1)^2}{1} = 0.415 \text{ V}$$

26. (a) On passing the current through the given cell Ag will oxidise to Ag^+ and Cu^{2+} will be reduced to Cu.

$$\frac{w}{E} = \frac{i \cdot t}{96500} = \frac{9.65 \times 3600}{96500}$$

$= 0.36$ eq. of $Ag^+ = 0.36$ mole of Ag^+

$= 0.36$ eq. of Cu^{2+}

$= \frac{0.36}{2}$ mole of Cu^{2+}

$\therefore \quad [Ag^+] = 1 + 0.36 = 1.36$ M

$[Cu^{2+}] = 1 - 0.18 = 0.82$ M

27. (a) For given cell in problem, the spontaneous reaction

$$E = E^o_{OP_{Ag}} + E^o_{RP_{Cu}} + \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Ag^+]^2}$$

Initially $Cu^{2+} = 1$ M and $Ag^+ = 1$ M

$\therefore \quad E_{cell} = E^o_{cell} = -0.474$

After electrolysis $Cu^{2+} = 0.82$ M, $Ag^+ = 1.36$ M.

$$\therefore \quad E_{cell} = E^o_{cell} + \frac{0.059}{2}\log\frac{0.82}{(1.36)^2}$$

$$= E^o_{cell} - 0.010 = -0.474 - 0.010 = -0.484 \text{ V}$$

E^o_{cell} is negative for $Ag^+ | Ag \| Cu^{2+} | Cu$ and is – 0.474 V.

Thus, E^o_{cell} for spontaneous cell reaction will be 0.474 V in first case and 0.484 V in II case.

28. (a) The decrease in free energy $= -\Delta G = nEF$

$2 \times 0.415 \times 96500 = 80095$ J $= 80.1$ kJ.

DPP 3.5

Subjective Type

1. Aqueous solution of brine contains Na^+, Cl^-, H^+ and OH^-. Electrode process are given below:

$2H^+ + 2e^- \rightarrow H_2$ (Cathode)

$2Cl^- \rightarrow Cl_2 + 2e$ (Anode)

Remaining solution will contain NaOH, which is base, therefore, pH will increase.

2. The given half-cell reactions are

(1) $BrO_3^- + 2H_2O + 4e^- = BrO^- + 4OH^- \quad E^o_1 = 0.54$ V

(2) $BrO^- + H_2O + e^- = \frac{1}{2}Br_2 + 6OH^- \quad E^o_2 = 0.45$ V

(3) $BrO_3^- + 3H_2O + 5e^- = \frac{1}{2}Br_2 + 6OH^- \quad E^o = ?$

Equation (3) can be generated by adding Eqs. (1) and (2). Hence

$$\Delta G^o_{(3)} = \Delta G^o_{(1)} + \Delta G^o_{(2)}$$

i.e., $-5FE^o = -4F(0.54 \text{ V}) - F(0.45 \text{ V})$

$$E^o = \frac{4(0.54 \text{ V}) + (0.45 \text{ V})}{5} = 0.522 \text{ V}$$

3. Daniell cell

$Zn(s)|Zn^{2+}\|Cu^{2+}|Cu(s)$

Anode: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

Cathode: $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

Cell reaction $Zn(s) + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu(s)$

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = E^o_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Above equation shows that the cell potential will decrease with increase in the concentration of Zn^{2+} ion.

4. (i) $$M^{n+} + ne^- \rightarrow M, E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]}$$

$$= E^o_{M^{n+}/M} + \frac{RT}{nF}\ln[M^{n+}]$$

Thus, electrode potential can be increased either by increasing metal ion concentrations, i.e., $[M^{n+}]$ or temperature *T*.

(ii) When equilibrium is reached in the cell reaction, E_{cell} becomes equal to zero. However, E^o_{cell} is a constant quantity. Hence, applying Nernst equation to the cell reaction, e.g. to the reaction:

$$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$$

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]} = E^o_{cell} - \frac{RT}{nF}\ln K_c.$$

At equilibrium $E_{cell} = 0$. Hence, $E^o_{cell} = \frac{RT}{nF}\ln K_c$.

(iii) (a) $\Delta G < 0$ (as redox reaction is spontaneous)

(b) $\Delta G > 0$ (as redox reaction is non-spontaneous).

5. When AgCl is added to a solution containing Br^- ions, the reaction to be considered is

$$AgCl(s) + Br^-(aq) \rightarrow AgBr(s) + Cl^-(aq)$$

The two half-cell reactions and cell reaction are

Reduction $\quad AgCl + e^- \rightarrow Ag + Cl^-$

Oxidation $\quad Ag + Br^- \rightarrow AgBr + e^-$

Cell reaction $\quad AgCl + Br^- \rightarrow AgBr + Cl^-$

The cell producing the above reactions is

$$Ag(s)|AgBr(s)|Br^-(aq)\|Cl^-(aq)|AgCl(s)|Ag(s)$$

Its standard emf would be

$$E^o_{cell} = E^o_{Cl^-|AgCl} - E^o_{Br^-|AgBr|Ag} = 0.222 \text{ V} - 0.095 \text{ V} = 0.127 \text{ V}$$

Now using the expression $\log K_{eq} = \dfrac{nFE^{o}_{cell}}{2.303\,RT}$

we get $\log K_{eq} = \dfrac{(1)(96500\text{ C})(0.127\text{ V})}{2.303(8.314\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K})}$

$= 2.148$

Hence, $K_{eq} = 140.6$

Let x be amount of Br^- that has converted to Cl^- at equilibrium. We have

$$K_{eq} = \frac{[Cl^-]}{[Br^-]} = \frac{x}{0.1\,M - x} = 140.6$$

Solving for x, we get $x = 0.0993$ M

Hence $[Cl^-] = 0.0993$ M and $[Br^-] = 0.1\text{ M} - 0.0993\text{ M}$

$= 0.0007$ M.

6. The given cell is $Ag|Ag^+$ (saturated Ag_2CrO_4 soln.)$||Ag^+$ (0.1M)$|Ag$

Cell Reaction Right half-cell $(Ag^+)_R + e^- \rightarrow Ag$

Cell reaction $Ag \rightarrow (Ag^+)_L + e^-$

$(Ag^+)_R \rightarrow (Ag^+)_L$

Cell potential $E_{cell} = -\dfrac{RT}{F}\ln\dfrac{[Ag^+]_L}{[Ag^+]_R}$

In the left half-cell, the concentration of Ag^+ will be related to the solubility product to Ag_2CrO_4 as shown in the following.

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}\ (aq)$$

If x is the solubility of Ag_2CrO_4 in solution, then

$[Ag^+] = 2x$ and $[CrO_4^{2-}] = x$

and $K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (2x)^2(x)$ or $x = (K_{sp}/4)^{1/3}$

$\Rightarrow [Ag^+]_L = 2x = 2(K_{sp}/4)^{1/3} = (2K_{sp})^{1/3}$

With its, the cell potential becomes $E_{cell} = -\dfrac{RT}{F}\ln\dfrac{(2K_{sp})^{1/3}}{[Ag^+]_R}$

Substituting the given data, we get

$$0.164\text{ V} = -(0.059\text{ V})\log\frac{(2\,K_{sp})^{1/3}}{(0.1\text{ M})}$$

or $\log(2\,K_{sp}/M^3)^{1/3} = -\dfrac{0.164}{0.059} + \log 0.1 = -3.78$

or $2\,K_{sp}/M^3 = \text{antilog}\,(-3 \times 3.78) = 4.75 \times 10^{-12}$

or $K_{sp} = 2.29 \times 10^{-12}\text{ M}^3$

Single Correct Answer Type

7. (b) For the given cell,

$$E = E^o - \frac{0.059}{2}\log_{10}\frac{[Mg^{2+}]}{[Zn^{2+}]}$$

This equation is of the form $y = mx + c$, its slope is negative and intercept equal to E^o.

Slope $= -\dfrac{0.059}{2}$; Intercept $= E^o$.

8. (b) When $\log Q = 0$, $E = E^o = 1.10$ V

The value of cell potential (E_{cell}) will decrease with increase in the value of $\log_{10} Q$; as indicated by the Nernst equation.

$$E = E^o - \frac{0.059}{n}\log_{10} Q$$

9. (d) Overall cell reaction is:

$$H_2(g) + 2Ag^+ \rightleftharpoons 2Ag(s) + 2H^+(aq)$$

$$E = E^o - \frac{0.06 \times 2.303}{2}\log\frac{[H^+]^2}{[Ag^+]^2 pH_2}$$

$$0.62 = 0.80 + \frac{2 \times 0.06 \times 2.303}{2}\log[Ag^+]$$

$[Ag^+] = 0.05$ M

Number of moles of Ag^+ in 100 mL $= \dfrac{MV}{1000} = \dfrac{0.05 \times 100}{1000}$

$= 0.005$

Mass of silver $= 0.005 \times 108$ g

Percentage of Ag in 1.08 g of alloy $= \dfrac{0.005 \times 108 \times 100}{1.08} = 50\%$

10. (a) Conductivity of ion Co^{2+} and $[Fe(CN)_6]^{4-}$

$= 2.06 \times 10^{-6} - 4.1 \times 10^{-7}\text{ohm}^{-1}\text{Cm}^{-1}$

$= 1.65 \times 10^{-6}\text{ohm}^{-1}\text{Cm}^{-1}$

$\therefore\ S = \dfrac{1.65 \times 10^{-6}}{616}$

$= 2.67 \times 10^{-9}\text{ mol/cm}^3 = 2.67 \times 10^{-6}$ mol/lt

$\therefore\ K_{sp} = 4s^3 = 7.69 \times 10^{-17}$.

11. (d) $AgCl(s) \rightleftharpoons Ag^+ + Cl^-$; $E^o = 0.22 - 0.80 = -0.58$ V

$$E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log[Ag^+/Cl^-]$$

$$0 = -0.58 - \frac{0.0591}{2}\log K_{sp}$$

On solving, $K_{sp} = 1.535 \times 10^{-10}\text{ M}^2$

12. (a) $E_{cell} = \dfrac{0.059}{2}\log\dfrac{[H^+]^2_{cathode} \times [P_{H_2}]_{anode}}{[H^+]^2_{anode} \times [P_{H_2}]_{cathode}}$

$$[OH^-] = \sqrt{CK_b} = \sqrt{0.1 \times 10^{-5}} = 10^{-3}\text{ M}$$

$$[H^+]_{anode} = \frac{10^{-14}}{10^{-3}} = 10^{-11}\text{ M}$$

$$[H^+]_{cathode} = \sqrt{CK_a} = \sqrt{0.1 \times 10^{-7}} = 10^{-4}\text{ M}$$

$$\therefore\ E_{cell} \doteq \frac{0.059}{2}\log\frac{(10^{-4})^2 \times 0.1}{(10^{-11})^2 \times 1} = 0.40\text{ V}$$

13. (c) $K = \text{Antilog}\left[\dfrac{nE^o}{0.059}\right]$

$= \text{Antilog}\left[\dfrac{2 \times 0.295}{0.059}\right] = 1 \times 10^{10}$.

Multiple Correct Answers Type

14. (a, c)

$Ca^{2+} + RH_2 \rightarrow CaR + 2H^+$

77.5 ppm = 77.5 g Ca^{2+} per 10^6 mL $= 77.5 \times 10^{-3}\text{ g L}^{-1}\ Ca^{2+}$

$= \dfrac{77.5 \times 10^{-3}}{40}\text{ mol L}^{-1}\ Ca^{2+}$ ion

$$= \frac{77.5 \times 10^{-3} \times 2}{40} \text{ mol L}^{-1} \text{ H}^+ \text{ ions}$$

$\therefore \quad [H^+] = 3.875 \times 10^{-3}$

$\therefore \quad pH = -\log (H^+) = 2.4$

15. (b, d)

The given cell is a concentration cell.

$Ag \rightarrow (Ag^+)_{LHE} + e$

$(Ag^+)_{RHE} + e \rightarrow Ag$

Net reaction: $(Ag^+)_{RHE} \rightarrow (Ag^+)_{LHE}$

$$E_{cell} = 0 - 0.0592 \log \frac{[Ag^+]_{LHE}}{[Ag^+]_{RHE}} = 0.0592 \log \frac{[Ag^+]_{RHE}}{[Ag^+]_{LHE}}$$

$$E_{cell} = 0.0592 \log \frac{[Ag^+]Ag_2C_2O_4}{[Ag^+]AgI}$$

In AgI solution, $[Ag^+] = K_{sp}\,(AgI)^{1/2}$

In $Ag_2C_2O_4$ solution, $[Ag^+]$

$$= 2 \times \left\{\frac{K_{sp}(Ag_2C_2O_4)}{4}\right\}^{1/3} = \left\{\frac{(2)K_{sp}(Ag_2C_2O_4)}{4}\right\}^{1/3}$$

$$= [2\,K_{sp}\,(Ag_2C_2O_4)]^{1/3}$$

16. (c, d)

RHE reaction: $Hg_2Cl_2(s) + 2e \rightarrow 2Hg(\ell) + 2Cl^-$

LHE reaction: $2Ag(s) + 2Cl^- \rightarrow 2AgCl(s) + 2e$

Net reaction: $Hg_2Cl_2(s) + 2Ag(s) \rightarrow 2Hg(\ell) + 2AgCl(s)$

In case of same concentration of Cl^- ions in the two half cells, E_{cell} is independent on the concentration of Cl^-. Other substances are either pure solids or liquids, which have unit activities irrespective of their amounts.

17. (a, b, c)

18. (a, b, c, d)

$$E_{cell} = E^o_{cell} - \frac{0.59}{2} \log \frac{[H^\oplus]^2}{[Zn^{2+}]p_{H_2}}$$

Check for $\dfrac{[H^\oplus]}{[Zn^{2+}]p_{H_2}} = 1$ for $E_{cell} = E^\ominus_{cell}$

It is possible in all cases.

Matching Column Type

19. (a → q), (b → r), (c → s), (d → p)

(a) $\Delta G^o_1 = -6F(-0.61)$

$\Delta G^o_2 = -2F(-0.76)$

$\Delta G^o_3 = -4F(E^o_3)$

$\Delta G^o_3 = \Delta G^o_1 - \Delta G^o_2$

$-4F\,E^o_3 = -6F(-0.61) - 2F(0.76)$

$-4E^o_3 = +3.66 - 1.52$

$$E^o_3 = -\frac{2.14}{4} = -0.535 \text{ V}$$

(b) $\Delta G^o_3 = -6F\,E^o_3 = -4F(0.45) + \{-2F(0.17)\}$

$$E^o_3 = \frac{1.8 + 0.34}{6} = 0.356 \text{ V}$$

(c) $-4F\,E^o_3 = -6F(1.45) - \{-2F(1.36)\}$

$$E^o_3 = \frac{+8.7 - 2.72}{4} = 1.47$$

(d) $-2F\,E^o_3 = -2F(0.80) - 2F(0.76)$

$E^o_3 = 0.80 + 0.76 = +1.56$ V

Integer Type

20. (8) $Pb + Hg_2SO_4 \rightarrow PbSO_4 + 2Hg$

ΔH (Heat of reaction)

$$\Delta H = -nF\left[R\left(\frac{\delta E}{\delta T}\right)_P - E\right]$$

$= 2 \times 96500\,[298(1.7 \times 10^{-4}) - 0.9467]$

$= -42.1$ kcal/mol

$\Delta G = -nFE$

$= -2 \times 96500 \times 0.9467$

$= -44.49$ kcal/mole

$\Delta G = \Delta H - T\Delta S$

$T\Delta S = \Delta H - \Delta G$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

$$= \frac{-42.1 - (-44.49)}{298}$$

$= -42.1 + 44.49$

$$= \frac{+2.39 \times 10^3}{298}$$

$= 8.02$ Ca K^{-1} mol^{-1}

21. (8)

For the reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

The reduction potential is $E = E^o - \dfrac{RT}{2F} \ln \dfrac{1}{[Cu^{2+}]}$

$$\therefore \quad 0.1335 = 0.34 \text{ V} - \left(\frac{0.059 \text{ V}}{2}\right) \log \frac{1}{[Cu^{2+}]}$$

$$\log \frac{1}{[Cu^{2+}]} = 7$$

$\Rightarrow \quad [Cu^{2+}] = 10^{-7}$

$\Rightarrow \quad K_{sp} = [Cu^{2+}][OH^-]^2$

$$\therefore \quad [OH^-]^2 = \frac{K_{sp}}{[Cu^{2+}]} = \frac{1 \times 10^{-19}}{10^{-7}} = 10^{-12}$$

$[OH^-] = 10^{-6}$ M

$$\therefore \quad [H^+] = \frac{k_w}{[OH^-]} = \frac{10^{-14}\text{ M}^2}{10^{-6}\text{ M}}$$

$[H^\oplus] = 10^{-8}$ M

pH = 8.

Comprehension Type

(a) In the given reaction,
Ag ions reduces to Ag and Glucose is oxidized to gluconic acid as per the given reaction.

$$Ag^+ + e^- \rightarrow Ag; \quad E^0_{red} = +0.800 \text{ V and}$$

$$\underset{\text{Gluconic acid}}{C_6H_{12}O_6 + H_2O \rightarrow C_6H_{12}O_7} + 2H^+ + 2e^-; \quad E^0_{ox} = -0.05 \text{ V}$$

Hence, $E^0_{cell} = 0.8 - 0.05 = 0.75$ V

$$\Delta G^0_{cell} = -nFE = -2F \times 0.75 = -RT \ln K$$

$$\Rightarrow \ln k = \frac{2F}{RT}(0.75) = 2 \times 38.92 \times 0.75 = 58.38$$

23. (c) For the reaction

$$C_6H_{12}O_6 + H_2O \rightarrow C_6H_{12}O_7 + 2H^+ + 2e^-;$$

$$E = E^\circ - \frac{0.0591}{n}\ln\frac{[P]}{[R]} = E^\circ - \frac{0.0591}{2}\ln[H^+]^2$$

$$E - E^\circ = -\frac{0.0591}{2} \times \ln(-pH) = 0.0591 \times 11 = 0.065$$

So, $E_{oxidation}$ increases over $E^0_{oxidation}$ by 0.65 V.

24. (d) During Tollen's test, oxidation of silver ion requires an alkaline medium. Under these conditions it forms insoluble silver oxide, hence to dissolve this oxide a complexing agent, ammonia is added, which brings silver ion as diamminosilver (I) ion. $Ag(NH_3)_2^+$.

CHAPTER 4

DPP 4.1

Subjective Type

1. (a) Rate of reaction = $\dfrac{\text{Change in pressure}}{\text{Time in min}}$

$$= \frac{2-1.2}{50} = \frac{0.8}{50} = 1.6 \times 10^{-2} \text{ atm min}^{-1}.$$

(b) $\because$ Change in molarity may be derived by

$$PV = nRT;\ \frac{n}{V} = \frac{P}{RT}$$

$$\Delta C = \frac{\Delta P}{RT} = \frac{0.8}{0.821 \times 298} = 0.0327$$

2. Rate of reaction = $\frac{1}{2}\times$ Rate of disappearance of A

$$= \frac{1}{2}\left(-\frac{\Delta[A]}{\Delta t}\right) = \frac{1}{2}\left[\frac{0.5-0.4}{10}\right] = 0.005 \text{ mol L}^{-1} \text{ minute}^{-1}.$$

3. Given concentration of H^+

$$[H^+] = \frac{3.0\times10^{-6}}{0.05} \times 10^3 \text{ mol L}^{-1}$$

$$= \frac{3.0\times10^{-1}}{5}$$

$\Rightarrow$ $= 0.06 \text{ mol L}^{-1}$

$\because$ Disappearance of 10^7 mol L^{-1} takes 1 sec

$\therefore$ Disappearance of 0.06 mol L^{-1} will take

$$\frac{1}{10^7} \times 0.06 = 6 \times 10^{-9} \text{ sec}$$

4.	$A_2(g) \rightarrow$	$B(g) +$	$\frac{1}{2}C(g)$
$t = 0$	100 mm	0	0
$t = 5$ m	$(100 - x)$	x	$\frac{x}{2}$

Total pressure = $100 - x + x + \frac{x}{2} = 120 \quad (x = 40)$

then Rate of disappearance of $A_2 = -\dfrac{d[A_2]}{dt} = \dfrac{40}{5} = 8$

Single Correct Answer Type

5. (d) Given, $r = -\dfrac{dP_A}{dt} = k' P_A^2$ atm/hr

and $r = -\dfrac{1}{V}\dfrac{dn_A}{dt} = kC_A^2 \text{ Mhr}^{-1}$

$\therefore\ k' P_A^2 = kC_A^2$

$$\Rightarrow\ k = k'\left(\frac{P_A}{C_A}\right)^2 = k'(RT)^2$$

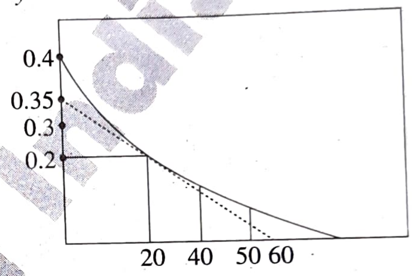
6. (b) $-\dfrac{1}{x}\dfrac{d[A]}{dt} = \dfrac{1}{y}\dfrac{d[B]}{dt}$

Taking log $\left[\dfrac{-d[A]}{dt}\right] = \log\left[\dfrac{d[B]}{dt}\right] + \log\dfrac{x}{y}$

Comparing $\log\left(\dfrac{x}{y}\right) = 0.3$

$\dfrac{x}{y} = 2$

7. (d)



Slope of graph at 20 sec = $\dfrac{dy}{dx} = \dfrac{0.35}{50} = 7\times10^{-3} \text{ ms}^{-1}$

8. (d) $-\dfrac{d[MnO_4^-]}{dt} = 4.56\times10^{-3}\text{ms}^{-1}$

$$-\frac{1}{2}\frac{d[MnO_4^-]}{dt} = +\frac{1}{5}\frac{d[I_2]}{dt}$$

$$\frac{d[I_2]}{dt} = \frac{5}{2}\left[-\frac{d[MnO_4^-]}{dt}\right]$$

$$\frac{d[I_2]}{dt} = \frac{5}{2}\times4.56\times10^{-3} = 11.4\times10^{-2}\text{ms}^{-1}$$

9. (c) $Zn + \text{Dil. } HCl \rightarrow ZnCl_2 + H_2\uparrow$

Average rate of reaction = $\dfrac{\text{Change in concentration of } H_2}{\text{Change in time}}$

$$= \frac{V_3 - 0}{40-0} = \frac{V_3}{40}$$

10. (b) Reaction occurring at smallest time interval is known as instantaneous rate of reaction, e.g., instantaneous rate of reaction at 40 s is rate of reaction during a small interval of time close to 40 s. Volume change during a small time interval close to 40 s i.e., 40 – 30 s, 50 – 40 s, 50 – 30 s, 40 – 20 s.

Instantaneous rate of reaction = $\dfrac{\text{Change in volume}}{\text{Time interval close to 40 s}}$

(a) $r_{\text{inst}}(20\text{ s}) = \dfrac{V_5 - V_2}{50-30}$ correct

(b) $r_{\text{inst}}(20\text{ s}) = \dfrac{V_4 - V_3}{50-30}$ incorrect, correct is $\dfrac{V_5 - V_3}{50-30}$

(c) $r_{\text{inst}}(10\text{ s}) = \frac{V_3 - V_2}{40 - 30}$ correct

(d) $r_{\text{inst}}(20\text{ s}) = \frac{V_3 - V_1}{40 - 20}$ correct

Multiple Correct Answers Type

11. (a, b)

$$\text{Rate} = \frac{-d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

12. (c, d)

(a) is wrong because rate constant is constant at constant temperature, (b) is wrong because rate depends upon $[H^+]^2$, (c) is correct because change in pH means change in $[H^+]$, (d) is correct because rate ∝ $[H^+]^2$

13. (a, c, d)

$$c = \frac{n}{V} \quad \therefore \quad \frac{dc}{dt} = \frac{1}{V}\frac{dn}{dt}$$

As $PV = nRT$, i.e., $P = \frac{n}{V}RT = cRT$

$$\text{or} \quad c = \frac{P}{RT} \quad \therefore \quad \frac{dc}{dt} = \frac{d}{dt}\left(\frac{P}{RT}\right) = \frac{1}{RT}\frac{dP}{dt}$$

14. (a, b, c)

$$\text{Rate} = \frac{1}{3}\frac{d[Br_2]}{dt} = -\frac{1}{5}\frac{d[Br^-]}{dt} \Rightarrow \frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$$

15. (b, c, d)

The instantaneous rate of the reaction can be expressed by any of the following expressions.

$$\frac{1}{2}\frac{-d[A]}{dt} \text{ or } \frac{-d[B]}{dt} \text{ or } \frac{d[A_2B]}{dt}$$

Integer Type

16. (2, 1 respectively)

$$\Delta I^{\ominus} = 0.25 - 0.23 = 0.02 \text{ mol L}^{-1}$$

$$\Delta t = 10 - 0 = 10 \text{ min}$$

$$-\frac{\Delta[I^{\ominus}]}{\Delta t} = \frac{(0.02)}{10} = 2 \times 10^{-3} \text{ mol L}^{-1}\text{min}^{-1}$$

$$= \frac{\Delta[I_2]}{dt} = -\frac{1}{2}\frac{\Delta[I^{\ominus}]}{dt} = \frac{0.002}{2} = 1 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}.$$

17. (6)

In the reaction,

$$N_2 + \underset{\substack{3\text{ mol}\\6\text{ g}}}{3H_2} \longrightarrow \underset{\substack{2\text{ mol}\\34\text{ g}}}{2NH_3}$$

∴ 34 g of NH_3 is formed by 6 g of H_2.

∴ Rate of disappearance of H_2 = 6 g hr^{-1}.

Comprehension Type

18. (b) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

$$-\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt} = \text{Rate of reaction}$$

19. (d) For the reaction, $m_1A + m_2B \rightarrow n_1C + n_2D$

$$-\frac{1}{m_1}\frac{d[A]}{dt} = +\frac{1}{n_1}\frac{d[C]}{dt}$$

$$-\frac{d[A]}{dt} \Big/ \frac{d[C]}{dt} = \frac{m_1}{n_1}$$

20. (b) In the reaction,

$$2SO_2(g) + \underset{\substack{1\text{ mol}\\32\text{ g}}}{O_2(g)} \rightarrow \underset{\substack{2\text{ mol}\\160\text{ g}}}{2SO_3(g)}$$

∵ 160 g of SO_3 is formed by 32 g of O_2.

∴ 100 g of SO_3 will be formed by $\frac{32}{160} \times 100$ or 20 g of O_2.

∴ Rate of disappearance of O_2 = 20 g min^{-1}.

DPP 4.2

Subjective Type

1. $r = k[A]^n$ Assume $r = x$ mole^{-1} sec^{-1}

k_1 = sec^{-1} k'_1 = sec^{-1}

k_2 = mole^{-1} lit sec^{-1} $k'_2 = 10^3 \times$ mole^{-1} ml sec^{-1}

k_3 = mole^{-2} lit^2 sec^{-1} $k'_3 = 10^6 \times$ mole^{-2} ml^{-2} sec^{-1}

Value of k'_1 = [Value of k'_2] × 10^{-3} = [Value of k'_3] × 10^{-6}

2. (a) $-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = K[NH_3]^0$

$$\therefore \quad \frac{d[N_2]}{dt} = K = 2.5 \times 10^{-4} \text{ Ms}^{-1}$$

$$\frac{d[H_2]}{dt} = 3K = 3 \times 2.5 \times 10^{-4} = 7.5 \times 10^{-4} \text{ Ms}^{-1}$$

(b) $-\frac{d[NH_3]}{dt} = \frac{K_1[NH_3]}{1 + K_2[NH_3]}$

if $[NH_3]$ is very very low $[1 + K_2[NH_3] \approx 1]$.

or $-\frac{d[NH_3]}{dt} = K_1[NH_3]$, i.e., Ist order reaction if $[NH_3]$ is very very high.

$$-\frac{d[NH_3]}{dt} = \frac{K_1}{\frac{1}{[NH_3]} + K_2} = \frac{K_1}{K_2} = K'\left[\frac{1}{[NH_3]} + K_2 \approx K_2\right]$$

i.e., zero order.

3. Rate = K [Reactant]^n

For Case I : Let a mole of reaction in vessel of V litres

$$\therefore \quad r_i = K\left[\frac{a}{V}\right]^n \qquad (1)$$

For Case II : The volume is doubled, rate becomes half.

$$\therefore \quad \frac{r_i}{2} = K\left[\frac{a}{2V}\right]^n \qquad (2)$$

∴ By Eqs. (1) and (2),

or $2 = (2)^n$ ∴ $n = 1$

Note: The above fact is not valid for solution phase reactions.

4. (i) From the first statement it may be deduced that the reaction is first order with respect to A. Since doubling both concentrations causes only a doubling of the rate, which is caused by the doubling of the A concentration, the doubling of the B concentration has had no effect on the rate; the rate is zero order with respect to B.
(ii) This reaction is pseudo first order. No matter how complete the reaction of the complex ion, the concentration of the water changes very little, and therefore it is impossible to determine the order with respect to water. Quantitatively, the concentration of water is about 55.5 M. If the reaction went to completion, the water concentration could not fall below 55.4 M. Less than 0.2% change is insufficient to allow a determination of how the water concentration affects the rate of reaction.

Single Correct Answer Type

5. (a) For reaction $C_6H_5N_2^+Cl^- \rightarrow C_6H_5Cl + N_2$
Let the rate law be

$$r = \frac{d[N_2]}{dt} = k[C_6H_5N_2^+Cl^-]^x$$

$$= k[\text{Salt}]^x \qquad \text{(i)}$$

From given, if $2r = \dfrac{2d[N_2]}{dt} = k(2[\text{salt}])^x$ (ii)

Then, on dividing (i) by (ii), we get

$$\frac{1}{2} = \left(\frac{1}{2}\right)^x \Rightarrow \boxed{x = 1}$$

∴ Reaction is of 1st order.

6. (a) For $A + B + C \xrightarrow{k} D$
Let the rate law be

$r = k[A]^x [B]^y [C]^z$ (i)
Ist change – $2r = k[A]^x (2[B])^y [C]^z$ (ii)
2nd change – $2r = k(2[A])^x (2[B])^y [C]^z$ (iii)
3rd change – $4r = k[A]^x (2[B])^y (2[C])^z$ (iv)

On dividing (i) by (ii),

$$\frac{1}{2} = \left(\frac{1}{2}\right)^y \Rightarrow \boxed{y = 1}$$

On dividing (ii) by (iii),

$$1 = \left(\frac{1}{2}\right)^x \Rightarrow \boxed{x = 0}$$

On dividing (ii) by (iv),

$$\frac{1}{2} = \left(\frac{1}{2}\right)^z \Rightarrow \boxed{z = 1}$$

∴ The rate expression $r = k[B]^1[C]^1[A]^0$
∴ Order = 1 + 1 + 0 = 2.

7. (a) It is fact.

8. (c) Order have no relation with stoichiometric coefficient.

9. (a) $A + B \rightarrow$ product

$r = K [A]^1 [B]^2$
$r_1 = K[1]^1 [1]^2 = 1 \times 10^{-2} \quad (K = 1 \times 10^{-2})$

$$r_1 = K\left[\frac{1}{2}\right]\left[\frac{1}{2}\right]^2 = 1 \times 10^{-2} \times \frac{1}{8} = 1.25 \times 10^{-3}$$

10. (c) Out of the given four statements, option (c) is not correct.
Order of Reaction
Order of reaction is equal to the sum of powers of concentration of the reactants in rate law expression.
For any chemical reaction

$xA + yB \rightarrow$ Product
Rate = $k\,[A]^x\,[B]^y$
Order = $x + y$

Order of reaction can be a fraction also. Order of reaction is not always equal to sum of the stoichiometric coefficients of reactants in the balanced chemical equation. For a reaction it may or may not be equal to sum of stoichiometric coefficient of reactants.

11. (d) **Rate law for**

Ist order — Rate = $K[A]^1$
IInd order — $R_2 = K[A]^2$
IIIrd order — $R_3 = K[A]^3$

than we can say $[A] = 1$ $r_1 = r_2 = r_3$
$[A] < 1$ then $r_1 > r_2 > r_3$
$\dot{y}\,[A] > 1$ then $r_3 > r_2 > r_1$

Multiple Correct Answers Type

12. (a, b)
Pseudo first order reaction is a chemical reaction in which rate of reaction depends upon concentration of only one reactant while concentration of another reactant has no effect on rate of reaction.

13. (b) The value of the rate constant for the same reaction changes with temperature.

14. (a, b, c)
Molecularity can be defined only for an elementary reaction. It has no meaning for the complex reaction.

15. (a, b, d)
The order of the inversion of sucrose is 1.

16. (b, c)
The rate of reaction will be halved on reducing the concentration of alkyl halide to half. The rate constant will also increase on increasing temperature.

Matching Column Type

17. (A) → (i), (ii), (iii), (iv) first order w.r.t. A,B
(B) → (ii), (iii), (iv) first order w.r.t. A and O w.r.t. B
(C) → (i), (ii), (iii), (iv) first order w.r.t. A and B
(D) → (iii), (iv) zero order w.r.t. A and B but stoichiometric coeff. are different

Integer Type

18. (3) Let the order of the reaction with respect to G and H be m and n, respectively. The given information are as follows:

$r = k[G]^m [H]^n$
$8r = k\{2[G]\}^m \{2[H]\}^n = 2^{m+n}(k[G]^m [H]^n) = 2^{m+n} r.$

Hence, $m + n = 3$.
[**Note:** It is also given that $2r = k\,\{2[G]\}^m [H]^n$
$= 2^m (k[G]^m [H]^n) = 2^n r]$
The gives $m = 1$. Hence, $n = 3 - m = 2$. Thus, the reaction is first order with respect to G and second order with respect to H and the overall order of the reaction is three.

19. (2)

$r = k[A]^m$ (i)
$2.25\, r = k[1.5\, A]^m$ (ii)

$$\frac{1}{2.25} = \left(\frac{1}{1.5}\right)^m \Rightarrow m = 2$$

Comprehension Type

20. (b) Let the rate law for the reaction

$A \rightarrow B + C$ be

$r = k\,[A]^n$

then $\dfrac{r_1}{r_2} = \left\{\dfrac{[A_1]}{[A_2]}\right\}^n$

$\Rightarrow \quad \left(\dfrac{0.17}{0.34}\right)^n = \left(\dfrac{0.05}{0.10}\right)$

$\Rightarrow \quad \left(\dfrac{1}{2}\right)^n = \dfrac{1}{2}$

$\Rightarrow \quad n = 1$

21. (a) From 1st experiment

$0.05 = k\,[0.170]^1$

$\Rightarrow \quad k = 0.294 \text{ L mol}^{-1}\text{ hr}^{-1}$

DPP 4.3

Subjective Type

1. The fraction of A and B remaining at any time t are

$$(f_A)_t = \frac{[A]_T}{[A]_0}$$

and $\quad (f_B)_t = \dfrac{[B]_t}{[B]_0}$

$\therefore \quad \ln(f_A)_t = -k_A t$

and $\quad \ln(f_B)_t = -k_B t$

$\therefore \quad \dfrac{k_A}{k_B} = \dfrac{\ln(f_A)_t}{\ln(f_B)_t} = \dfrac{\ln(0.01)}{\ln(0.99)} = 458$

2. $$Cl_2O_7 \longrightarrow Cl_2 + \frac{7}{2}O_2$$

Mole at $t = 0$	a	0	0
Mole at $t = 55$ sec	$(a - x)$	x	$7x/2$

(a) Since, pressure of Cl_2O_7 is given and therefore,

$a \propto 0.062$

$(a - x) \propto 0.044$

$\because \quad k = \dfrac{2.303}{t}\log_{10}\dfrac{a}{a-x} \qquad \therefore \quad K = \dfrac{2.303}{55}\log_{10}\dfrac{0.062}{0.044}$

$k = 6.23 \times 10^{-3}\text{ sec}^{-1}$

(b) Let at $t = 100$ sec, $(a - x) \propto P$

$\therefore \quad 6.23 \times 10^{-3} = \dfrac{2.303}{100}\log_{10}\dfrac{0.062}{P} \qquad \therefore \quad P = 0.033$ atm.

3. $k = \dfrac{2.303}{t}\log\dfrac{R_0}{R}$

$\log\dfrac{R_0}{R} = \dfrac{2.2 \times 10^{-5} \times 90 \times 60}{2.303} = 0.0515$

$\Rightarrow \quad \dfrac{R_0}{R} = 1.12 \quad \Rightarrow \quad R_0 = 1.12\,R$

% decomposed = 11.2 %

[% $a = 1 - e^{-kt} \times 100$]

4. We have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.4 \times 60 \times 60\text{ s}} = 8.02 \times 10^{-5}\text{ s}^{-1}$$

(a) Now using the expression $\log\dfrac{m}{m_0} = -\dfrac{k}{2.303}t$, we get

$$\log\frac{m}{10\,g} = -\left(\frac{8.02 \times 10^{-3}\,s^{-1}}{2.303}\right)(9.6 \times 60 \times 60\,s) = -1.2035$$

or $\dfrac{m}{10\text{g}} = 0.0625$ or $m = 0.625$g

(Note that 9.6 h is half life, hence, $m = m_0/2^4 = 10$ g/16 $= 0.625$ g.)

(b) Using the expression $\log\dfrac{N}{N_0} = -\dfrac{k}{2.303}t$, we get

$$t = -\frac{2.303}{k}\log\frac{N}{N_0}$$

$$= -\frac{2.303}{(8.02 \times 10^{-5}\text{ s}^{-1})}\log\left(\frac{1.0 \times 10^8}{5.0 \times 10^{10}}\right) - 77503\text{ s}$$

$\equiv 21.52$ h.

Single Correct Answer Type

5. (c) All the three plots are correct.

(I) log $(a - x)$, where $(a - x)$ is remaining concentration, decreases with passage of time.

(II) $k = \dfrac{2.303}{t}t_{\log 10}\left(\dfrac{a}{a-x}\right)$

$$\log\left(\frac{a}{a-x}\right) = \frac{k}{2.303} \times t$$

$$y = m \times x$$

Plot of log $\left(\dfrac{a}{a-x}\right)$ against 't' gives straight line through origin.

(III) $t_{1/2} = \dfrac{0.693}{k}$; Half-life of first order reaction does not depend on initial concentration. Thus, graph of $t_{1/2}$ against 'a' gives horizontal straight line.

6. (b) For 2nd order reaction

$$\frac{1}{[A_t]} = kt + \frac{1}{[A_o]}$$

Comparing with $y = mx + c$

Slope $= \tan\theta = k = 0.6$

Intercept $=$ OC $= \dfrac{1}{[A_o]} = 2 \Rightarrow [A_o] = \dfrac{1}{2}$

$\therefore \quad r = k[A_o]^2 = 0.6 \times \dfrac{1}{4} = 0.150\text{ mol L}^{-1}\text{ min}^{-1}$

7. (b) $C = C_0\,e^{-kt}$

$\therefore \quad \log C = -kt\log e + \log C_0$

$$\log C = \left(\frac{-k}{2.303}\right)(t) + \log C_0$$

$$\text{slope} = \frac{-k}{2.303}.$$

8. (b) After 1 hr, $n = \dfrac{60}{10} = 6$

$$\therefore \quad \frac{C}{C_0} = \left(\frac{1}{2}\right)^6 = 64$$

9. (b) $\dfrac{C_A}{C_{A_0}} = \left(\dfrac{1}{2}\right)^{t/t_{1/2}{}^{1}}$

$$\frac{C_B}{C_{B_0}} = \left(\frac{1}{2}\right)^{t/t_{1/2}{}^{2}}$$

$$\frac{C_A}{4C_{B_0}} = \left(\frac{1}{2}\right)^{t/5}$$

$$\frac{C_B}{C_{B_0}} = \left(\frac{1}{2}\right)^{t/15}$$

$$\frac{1}{4}\left(\frac{1}{2}\right)^{t/15} = \left(\frac{1}{2}\right)^{t/5}$$

$$\left(\frac{1}{2}\right)^{\frac{t}{15}+2} = \left(\frac{1}{2}\right)^{t/5}$$

$$\frac{t}{15} + 2 = \frac{t}{5}$$

$$\Rightarrow \quad \frac{2t}{15} = 2 \quad \Rightarrow \quad \mathrm{t = 15\ min}$$

10. (b) Order of reaction is 2 (from unit of K).

$\therefore$ Rate = $\mathrm{KC_A^2}$

$$\mathrm{C_A} = \sqrt{\frac{1/12 \times 10^{-5}}{2 \times 10^{-4}}} = \sqrt{\frac{1}{24} \times 10^{-1}} = \sqrt{\frac{1}{240}}$$

$$= \sqrt{\frac{5}{1200}} = \frac{1}{20}\sqrt{\frac{5}{3}}\ \mathrm{M}$$

11. (b) No. of half life = $\dfrac{60}{10}$ = 6 half life.

$$C_t = \frac{C_0}{(2)^n} = \frac{Co}{(2)^6} = \left(\frac{C_0}{64}\right)$$

$$k = \frac{2.303}{t}\log\left(\frac{100}{100 - x\%}\right)$$

$$\frac{k_1}{k_2} = \left(\frac{t_2}{t_1}\right)\frac{\log\left(\frac{100}{10}\right)}{\log\left(\frac{100}{1}\right)}$$

$$\frac{k_1}{k_2} = 2\frac{\log 10}{2\log 10} = 1$$

Multiple Correct Answers Type

12. (a, b)

For a particular reaction, the rate constant is independent of concentration and time.

13. (a, b, d)

For a first order reaction $t_{1/2} = \dfrac{0.693}{k}$

i.e., half life of the reaction is independent of the initial concentration of the reactant.

14. (a, b)

$t_{99.9\%} = 10t_{1/2}$, $t_{96.87\%} = 5t_{1/2}$

15. (a, c) Amount of the substance left after n half-lives:

Amount of the substance left after one half-life = $\dfrac{[A_0]}{2}$

Amount of the substance left after two half-life = $\dfrac{1}{2}\dfrac{[A_0]}{2} = \dfrac{[A_0]}{2^2}$

Amount of the substance left after three half-life

$$= \frac{1}{2} \times \frac{[A_0]}{2^2} = \frac{[A_0]}{2^3}$$

Amount of the substance left after n half-life = $\dfrac{[A_0]}{2^n}$

and Avg. life (τ) = $\dfrac{1}{k} = \dfrac{t_{1/2}}{0.693} = 1.44 \times t_{1/2}$

16. (a, c)

$$k = \frac{1}{t}[p_o - p_A] \quad \text{and} \quad t_{1/2} = \frac{p_o}{2k}$$

where p_o is initial pressure of A and p_A is the pressure of A after time t.

Further, $p_o - p_A = p$, decrease in pressure of A in time t. Hence, we can also write

$$k = \frac{p}{t} \quad \text{or} \quad p = kt \quad \text{or} \quad p \propto \mathrm{t}$$

Matching Column Type

17. (A → 2), (B → 3), (C → 1), (D → 4)

For zero order reactions $[A]_t = [A]_o - kt$

For second order reactions $\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_o}$

For third order reactions

$$kt = \frac{1}{(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right] (here\ n = 3)$$

Differentiating w.r.t. t

$$kt = \frac{1}{(n-1)}\left[\frac{d}{dt}(a-x)^{1-n} - 0\right]$$

$$k = \frac{1}{n-1}(1-n)(a-x)^{-n}\left(-\frac{dx}{dt}\right)$$

$$k = \frac{1}{(n-1)}\frac{n-1}{(a-x)^n}\frac{dx}{dt}$$

Taking log :

$$\log k = \log 1 - \log (a-x)^n + \log\frac{dx}{dt}$$

$$\log k = -n\log(a-x) + \log\frac{dx}{dt}$$

$$\log\frac{dx}{dt} = \log k + n\log(a-x)$$

Comparing with $y = c + mx$, $m = 3$

$\tan\theta = 3$

$\therefore \quad \theta = 71.55°$

For half order reactions

$$[A_t]^{1/2} = [A_0]^{1/2} - \frac{kt}{2}$$

Integer Type

18. (4) $\log \frac{dx}{dt} = \log k + \log (a-x)^n$

Comparing with $y = mx + c$

$c = \log k = 0.6021$

$\therefore \quad k = 4$

19. (5) A general expression for the half life ($t_{1/2}$) is given by $t_{1/2} \propto \frac{1}{a^{n-1}}$; where n is order of the reaction.

$$(t_{1/2})_1 \propto \frac{1}{a^{n-1}}$$

$$(t_{1/2})_2 \propto \left(\frac{2}{a}\right)^{n-1} \Rightarrow \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{1}{2}\right)^{n-1} \Rightarrow \frac{1}{16} = \left(\frac{1}{2}\right)^{n-1}$$

$\therefore \quad n = 5.$

Comprehension Type

20. (b) $t_{1/2} = \frac{0.693}{K} = \frac{0.693}{1.2 \times 10^2} \times 2.303$

$= 2.5 \times 10^{-3}$ sec

21. (a) After 5×10^{-3} sec.

$[N_2O_5] = \frac{0.2}{2} e^{-1.2 \times 10^2 \times 2.303 \times 5 \times 10^{-3}}$

$= 0.025$ M

$\therefore$ rate $= 0.025 \times 1.2 \times 10^2 \times 2.303$

$= 6.94$ mol/lt. sec.

DPP 4.4

Subjective Type

1. Let rate $= k\,[HgCl_2]^a\,[K_2Cr_2O_7]^b$

So from exp. (1)

$\frac{0.0068}{65} = k\,[0.0836]^a\,[0.404]^b$ (1)

from exp. (2)

$\frac{0.0031}{120} = k\,[0.0418]^a\,[0.404]^b$ (2)

from exp. (3)

$\frac{0.0032}{60} = k\,[0.0418]^a\,[0.404]^b$ (3)

from (1) and (2)

$4 = 2^b$ or $(2)^2 = (2)^b$

$\Rightarrow \quad b = 2$

from (1) and (3)

$2 = 2^b$ or $a = 1$

so overall order = 2 + 1 = 3

rate $= k\,[HgCl_2]^2\,[K_2C_2O_4]$

2. Rate $= K\,[A]^m\,[B]^n$

For Case I: $0.05 = K[0.1]^m\,[0.2]^n$ (1)

For Case II: $0.10 = K[0.2]^m\,[0.2]^n$ (2)

For Case III : $0.05 = K[0.1]^m\,[0.1]^n$ (3)

By Eqs. (1) and (2), $\frac{1}{2} = \left(\frac{1}{2}\right)^m$ $\quad \therefore m = 1$

By Eqs. (1) and (3), $1 = \left(\frac{1}{2}\right)^n$ $\quad \therefore n = 1$

Thus, rate $= K[A]^1\,[B]^0$ $\quad \therefore$ O.R. = 1 + 0 = 1

Now $0.05 = K[0.1]^1\,[0.2]^0$

$\therefore \quad K = \frac{0.05}{0.1} = 0.5\ \text{sec}^{-1}$

For I order reaction, $t_{1/2} = \frac{0.693}{K} = \frac{0.693}{0.5} = 1.386\ \text{sec}^{-1}$.

3. Let the rate expression

$r = K[NO]^m\,[H_2]^n$ (1)

Case I: $[NO] \times 10^{-4} = 1.5 \quad \therefore [NO] = 1.5 \times 10^4$

$[H_2] \times 10^{-3} = 4.0 \quad \therefore [H_2] = 4.0 \times 10^3$

$-\frac{1}{2}\frac{d[NO]}{dt} \times 10^{-4} \quad \therefore -\frac{1}{2}\frac{d[NO]}{dt} = 4.4 \times 10^4$

$\therefore$ By Eqs. (1), $4.4 \times 10^4 = K[1.5 \times 10^4]^m\,[4.0 \times 10^3]^n$ (2)

Similarly for cases II and III, we can write

Case II: $2.2 \times 10^4 = K[1.5 \times 10^4]^m\,[2.0 \times 10^3]^n$ (3)

Case III: $0.24 \times 10^4 = K[0.5 \times 10^4]^m\,[2.0 \times 10^3]^n$ (4)

By Eqs. (2) and (3), $2 = (2)^n$ $\quad \therefore n = 1$

By Eqs. (3) and (4), $9.16 = (3)^m$ $\quad \therefore m = 2$

$\therefore$ O.R. with respect to NO is 2 and with respect to $H_2 = 1$

For rate constant use Eq. (2) with $m = 2$ and $n = 1$.

$$4.4 \times 10^4 = K[1.5 \times 10^4]^2\,[4.0 \times 10^3]^1$$

$\therefore \quad K = 4.88 \times 10^{-8}\ \text{mol}^{-2}\,L^2\,\text{min}^{-1}$.

4. Inspection of the given data indicates that on doubling the concentration of A keeping that of B constant increases the initial rate of reaction to two fold. This implies that the reaction is first-order with respect to A. On the other hand, doubling the concentration of B keeping that of A constant to B. This implies that the reaction is zero-order with respect to B. Hence, the expression of rate of reaction is

Rate $= k\,[A]^1\,[B]^0 = k\,[A]$

that is, the reaction is first-order with respect to A only.

To determine the half-life of A, we determine the rate constant using the above expression. Hence,

$$k = \frac{(\text{rate})_0}{[A]_0} = \frac{0.005\ \text{mol}\ L^{-1}\ \text{min}^{-1}}{0.01\ \text{mol}\ L^{-1}} = 0.5\ \text{min}^{-1}.$$

Hence, $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.5\ \text{min}^{-1}} = 1.386$ min.

Single Correct Answer Type

5. (b) $r = k\,[A]^x\,[B]^y$

$1.6 \times 10^{-4} = k\,[0.5]^x\,[0.5]^y$ (1)

$3.2 \times 10^{-4} = k\,[0.5]^x\,[1.0]^y$ (2)

$3.2 \times 10^{-4} = k\,[1.0]^x\,[1.0]^y$ (3)

(2) ÷ (1) $\quad 2 = 2^y \quad \Rightarrow \quad y = 1$

(3) ÷ (2) $\quad 1 = 2^x \quad \Rightarrow \quad x = 0$

$r = k\,[A]^\circ\,[B]^1 \quad \Rightarrow \quad r = K[B]$

6. (b) Rate = $k[A]^n$ (i)

$1.837 \times \text{Rate} = k[1.5\,A]^n$ (ii)

Dividing equation (ii) by (i),

$1.837 = 1.5n$

$\therefore\ n = 3/2$ (Solving by logarithmic method)

7. (b) Rate = $k[\text{HI}]^n$

$11 \times 10^{-8} = k[0.2]^n$ (i)

$2.75 \times 10^{-8} = k[0.1]^n$ (ii)

Dividing eq. (i) by eq. (ii),

$4 = 2^n,\ n = 2$

8. (b) When A is taken excess, its concentration will become constant; the rate law may, therefore, be given as:

Rate = $k[B]^2 \Rightarrow$ Order = 2

9. (d) Rate law equation is given by

$$\frac{dC}{dt} = k[A]^x[B]^y$$

$\therefore\ \frac{dC}{dt}$ for C at various concentration are

$1.2 \times 10^{-3} = k(0.1)^x(0.1)^y$ (i)

$1.2 \times 10^{-3} = k(0.1)^x(0.2)^y$ (ii)

$2.4 \times 10^{-3} = k(0.2)^x(0.1)^y$ (iii)

Solving for x [divide Eq. (iii) by Eq. (i)]

$$\frac{2.4\times10^{-3}}{1.2\times10^{-3}} = \frac{k(0.2)^x(0.1)^y}{k(0.1)^x(0.1)^y}$$

$2 = (2)^x$

$\Rightarrow\ x = 1$

Solving by y [divide Eq. (iii) by Eq. (i)]

$$\frac{2.4\times10^{-3}}{1.2\times10^{-3}} = \frac{k(0.2)^x(0.1)^y}{k(0.1)^x(0.1)^y}$$

$$2 = (2)^x\left(\frac{0.1}{0.2}\right)^y$$

$1 = (0.5)^y$

$(1)^0 = (0.5)^y$

$\Rightarrow\ y = 0$

Thus, $\frac{dC}{dt} = k[A]^1[B]^0$

$\Rightarrow\ \frac{dC}{dt} = k[A]^1$

10. (a) From experiments 1 and 4 (when $[A]_0$ is same), when $[B]_0$ is doubled, rate becomes 8 times. Thus, rate $\propto [B]^3$.
From experiments 1 and 3 (when $[B]_0$ is same), when $[A]_0$ is doubled, rate remains same. Thus rate $\propto [A]^0 \Rightarrow$ Rate = $k[A]^0[B]^3$.

11. (c) Let the rate of the reaction is

$r = k[A]^x[B]^y$

$r_1 = 3.0\times10^{-3} = k[0.25]^x[0.25]^y$ (i)

$r_2 = 6.0\times10^{-3} = k[0.5]^x[0.25]^y$ (ii)

$r_3 = 1.20\times10^{-2} = k[0.5]^x[0.5]^y$ (iii)

Divide equation (ii) by (i)

$$\frac{6.0\times10^{-3}}{3.0\times10^{-3}} = \frac{k[0.5]^x[0.25]^y}{k[0.25]^x[0.25]^y}$$

$(2)^1 = (2)^x \Rightarrow x = 1$

Divide equation (iii) by (ii)

$$\frac{1.20\times10^{-2}}{6.0\times10^{-3}} = \frac{k[0.5]^x[0.5]^y}{k[0.5]^x[0.25]^y}$$

$\therefore\ (2)^1 = (2)^y \Rightarrow y = 1$

$\therefore\ r = k[A]^1[B]^1$

Total order = 1 + 1 = 2.

Multiple Correct Answers Type

12. (b, c)
In experiments I and II, $[B]$ is constant and $[A]$ is doubled. The rate does not change, so order w.r.t. $[A]$ = zero.

Let rate = $k[A]^0[B]^x$

$r_2 = 0.002\ \text{Ms}^{-1} = k[0.1]^x$

$r_3 = 0.008\ \text{Ms}^{-1} = k[0.2]^x$

$\frac{r_3}{r_2} = 4 = (2)^x$

$\therefore\ (2)^2 = (2)^x$

$x = 2.$

So, order w.r.t. $[B] = 2$

Rate = $k[A]^0[B]^2$.

13. (b, c, d)
For experiments (3) and (2), $[A]$ is constant and $[B]$ is doubled and rates becomes 8 times, so order w.r.t. $[B] = 3$.
From experiments (1) and (3), $[B]$ is constant and $[A]$ is doubled, but rate does not change, so order w.r.t. $[A] = 0$.
Thus, rate = $k[B]^3$.

14. (a, c, d)
In experiment (1) and (3), $[A]$ is constant and $[B]$ becomes double, but rate does not change, so, order w.r.t. $B = 0$.
In experiment (1) and (2), $[B]$ is constant and $[A]$ is double and the rate also is doubled.
So, order w.r.t. $[A] = 1$.

15. (a, b, c)

$r_1 = k[A]^x[B]^y[C]^z$

$r_2 = 2r_1 = k[A]^x[2B]^y[C]^z$

$r_3 = 2r_1 = k[2A]^x[2B]^y[C]^z$

$r_4 = 4r_1 = k[A]^x[2B]^y[2C]^z$

Solve for x, y and z, $x = 0$, $y = 1$, $z = 1$

Order w.r.t. $[A] = 0$, $[B] = 1$, $[C] = 1$

Total order = 0 + 1 + 1 = 2

$r = k[A]^0[B][C]$.

16. (a, c, d)
On comparing exp. 1 and 2, keeping conc. of $[CH_3COCH_3]$ and $[H^+]$ same and on doubling conc. of $[Br_2]$, rate remains same.
$\Rightarrow$ Order w.r.t. $[Br_2]$ is 0.
On comparing exp. 2 and 3, keeping conc. of $[Br_2]$ and $[CH_3COCH_3]$ constant and doubling conc. of $[H^+]$, rate gets doubled.
$\Rightarrow$ Order w.r.t. $[H^+]$ is 1.
Divide Exp 4 by Exp 1, we get

$$\frac{[0.05]^0[0.4]^x[0.20]^1}{[0.05]^0[0.3]^x[0.05]^1} = \frac{3.1\times10^{-4}}{5.7\times10^{-5}}$$

$$\left(\frac{4}{3}\right)^x \times 4 = 5.44$$

$$\left(\frac{4}{3}\right)^x = 1.359$$

$\therefore\ (1.33)^x = (1.359) \Rightarrow x = 1$

$\Rightarrow$ Order w.r.t $[CH_3COCH_3]$ is 1.

Conclusion

$$r = k[Br_2]^0[CH_3COCH_3]^1\,[H^+]^1$$

Matching Column Type

17. (a → q), (b → p), (c → p), (d → r, s)

(a → q): Zero order reaction does not depend upon the concentration of reactants.

(b → p): Rate = $k[A]^1\,[B]^1$, i.e., order = 1 + 1 = 2

(c → p): Rate = $k[A]^{3/2}\,[B]^{1/2}$, i.e., order $= \frac{3}{2} + \frac{1}{2} = \frac{4}{2} = 2$

(d → r, s): When $[A]$ is in excess, $[A] = 0$, OR = 1.
When $[B]$ is in excess, $[B] = 0$, OR = 2.

Integer Type

18. (6) From experiments I and IV, it may be noted that $[B]$ is same but $[A]$ has been made four times, the rate of reaction has also become four times. This means that w.r.t. A,

Rate $\propto$ [A] (i)

From experiments II and III, it may be noted that $[A]$ is kept same and $[B]$ has been doubled, the rate of reaction has become four times. This means that w.r.t. B,

Rate $\propto [B]^2$ (ii)

Combining (i) and (ii), we get the rate law for the given reaction as:

Rate = k $[A]\,[B]^2$

Thus, order w.r.t. A = 1, order w.r.t. B = 2 and overall order of the reaction = 1 + 2 = 3

The rate constant and its units can be calculated from the data of each experiment using the expression.

$$k = \frac{\text{Rate}}{[A][B]^2} = \frac{\text{mol L}^{-1}\text{ min}^{-1}}{(\text{mol L}^{-1})(\text{mol L}^{-1})^2} = \text{mol}^{-2}\text{L}^2\text{ min}^{-1}$$

Expt.	**k (mol^{-2} L^2 min^{-1})**	**Expt.**	**k (mol^{-2} L^2 min^{-1})**
I	$\frac{6.0\times10^{-3}}{0.1\times(0.1)^2} = 60$	III	$\frac{2.88\times10^{-1}}{0.3\times(0.4)^2} = 6.0$
II	$\frac{7.2\times10^{-2}}{0.3\times(0.2)^2} = 6.0$	IV	$\frac{2.4\times10^{-2}}{0.4\times(0.1)^2} = 6.0$

$\therefore$ Rate constant, $k = 6.0$ mol^{-2} L^2 min^{-1}

9. (2) Rate = $k[\text{HI}]^n$

$$2.75\times10^{-8} = k[0.1]^n \quad \text{(i)}$$

$$11\times10^{-8} = k[0.2]^n \quad \text{(ii)}$$

Dividing equation (ii) by (i),

$$4 = 2^n \Rightarrow n = 2.$$

Comprehension Type

20. (b) $a = 100$
$t = 15$
$a + x = 200$

I set $\therefore K = \frac{2.303}{t}\log\left(\frac{a+x}{a}\right) = \frac{2.303}{15}\log\frac{200}{100}$

II set $\therefore K = \frac{2.303}{30}\log\left(\frac{400}{100}\right) = 0.046$ min

It is of first order.

21. (a) It is a fact.

22. (a) Rate = 100 × 0.046 = 4.6

DPP 4.5

Subjective Type

1.

	A	→	Product
$t = 0$	a		0
$t = 60$ min	$0.8a$		
$t = 90$ min	$0.40a$		
$t = 100$ min	$0.10a$		

In absence of catalyst

$$K = \frac{2.303}{60}\log\frac{a}{0.8a} = \frac{2.303}{60}\log\left(\frac{5}{4}\right) \quad \text{(i)}$$

For 1st catalyst

$$(K_{\text{cat.}})_{1\text{st}} = \frac{2.303}{30}\log\left(\frac{0.8a}{0.40a}\right) = \frac{2.303}{30}\log 2$$

$$\frac{(K_{\text{cat}})_{1\text{st}}}{K} = \frac{\frac{2.303}{30}\log 2}{\left(\frac{2.303}{60}\right)\times\left(\frac{5}{4}\right)} = \frac{2\log 2}{\log 5 - \log 4} = \frac{2\times0.30}{0.1}$$

$$\frac{(K_{\text{cat}})_{1\text{st}}}{K} = 6.21$$

$$\frac{(K_{\text{cat}})_{1\text{st}}}{K} = e^{\left(\frac{E_a - E_a^1}{RT}\right)}$$

$$6.21 = e^{\left(\frac{E_a - E_a^1}{RT}\right)}$$

$$2.303 \log 6.21 = \frac{80 - E_a^1}{RT}$$

$$E_a = 80 - \frac{2.303\times0.793\times8.314\times300}{1000}$$

$$= 80 - 4.56 = 75.44 \text{ kJ}.$$

2. (i) According to collision theory apart from the energy considerations, the colliding molecules should also have proper orientation for effective collision.
This condition might not be getting fulfilled in the reaction as it shows the number of reactants taking part in a reaction, which can never be zero.

(ii) No, the molecularity can never be zero or a fractional number as it shows the number of reactants taking part in a reaction which can never be zero.

3. Because activation energy of the reaction is very high at room temperature but at high temperature H—H and O—O bond break and colliding particles cross the energy barrier. This is why reaction between $H_2(g)$ and $O_2(g)$ does not lead to formation of water at room temperature while keeping in the same vessel.

4. For Ist order reaction, $K = \frac{0.693}{t_{1/2}}$

(a) $\therefore$ At 27°C $K_1 = \frac{0.693}{30} = 2.31 \times 10^{-2}$ minute^{-1}

$\therefore$ At 47°C $K_2 = \frac{0.693}{10} = 6.93 \times 10^{-2}$ minute^{-1}

(b) Now, $2.303 \log_{10} \frac{K_2}{K_1} = \frac{E_a}{R} \frac{[T_2 - T_1]}{T_1 T_2}$

$$\therefore\ 2.303 \log_{10} \frac{6.93 \times 10^{-2}}{2.31 \times 10^{-2}} = \frac{E_a}{8.314} \times \frac{[320 - 300]}{320 \times 300}$$

$\therefore$ $E_a = 43850$ J mol^{-1} or $E_a = 43.85$ kJ mol^{-1}

(c) For a reaction $E_{aF.R.} - E_{aB.R.} = \Delta H$

$\therefore$ $43.85 - E_{aB.R.} = -50.0$

or $E_{aB.R.} = 43.85 + 50.0 = 93.85$ kJ mol^{-1}

5. $K^{-1} = 0.639/360$ min^{-1} at 653 K and

$E_a = 200 \times 10^3$ J, $K_2 = ?$ at 723 K, $R = 8.314$ J

$\therefore$ From $2.30 \log_{10} (K_2/K_1) = (E_a/R)[(T_2 - T_1)/(T_1 T_2)]$

$K_2 = 0.068$ min^{-1}

Now, $t = \frac{2.303}{0.068} \log_{10} \frac{100}{25} = 20.39$ minutes.

Single Correct Answer Type

6. (c) Rate of enzyme catalysis increases with temperature but it decreases above 45°C because above 45°C, denaturation of enzymes take place.

7. (d) According to Arrhenius equation, $A\,e^{E_a/RT}$ the rate constant increases exponentially with temperature.

8. (d) It is fact.

9. (c) $\frac{k_{T+n\times10}}{k_T} = 2^n$

$\therefore$ $\frac{k_{T+50}}{k_T} = 2^5 = 32$ times.

10. (d) $E_a = 41570 \times R = 41570 \times 8.31 = 345612.98$ J

11. (c) $\log\left(\frac{K_2}{K_1}\right) = \frac{E_a}{2.303R} \frac{(T_2 - T_1)}{T_1 T_2} = \frac{65 \times 10^3 \times (298 - 273)}{2.303 \times 8.3 \times 298 \times 273}$

By calculation we find $\frac{K_2}{K_1} = 11$

12. (d) At equilibrium, Rate of forward reaction = Rate of backward reaction.

13. (c) $\Delta H = E_f - E_b = -40$ kJ mol^{-1}, since $E_f/E_b = 2/3$,

we get $E_f = 2E_b/3$

Thus, $(2E_B/3) - E_b = -40$ kJ mol^{-1}.

This gives $E_b = 120$ kJ mol^{-1}

and $E_f = (2/3)E_b = (2/3)$ (120 kJ mol^{-1}) = 80 kJ mol^{-1}.

14. (b) We have $\ln \frac{k'}{k} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{E_a}{R} \frac{\Delta T}{T_1 T_2}$

For ΔT positive, k'/k increases faster with larger value of activation energy. Hence, $(k_1'/k_1) > (k_2'/k_2)$.

15. (b) As $\frac{1}{T}$ increase (T decreases) log K or K increases.

Thus, given reaction is exothermic i.e., $\Delta H^o A < 0$

$$\log_e K = \frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

Thus, slope is $\frac{\Delta H^o}{R}$ and $\Delta A^o = \frac{\Delta S^o}{R}$.

Multiple Correct Answers Type

16. (b, d)

$k = Ae^{-\Delta E/RT}$

$\log k = \log A - \frac{\Delta E}{RT}$

$\frac{d}{dt}(\log k) = -\frac{\Delta E}{R} \cdot \frac{-1}{T^2} = \frac{\Delta E}{RT^2}$.

17. (a, b, c)

From the question $\frac{E_a}{R} = 1.25 \times 10^4$

$E_a = 1.25 \times 10^4 \times 1.98 \times 10^{-3} = 24.83$ kcal.

18. (a, d)

When $Ea_{(f)} > Ea_{(b)}$

Then reaction is endothermic.

Now $\Delta E = E_f - E_b$

$= 50 - 30$

$= 20$ kJ.

19. (a, d)

When the reactant molecules collide with each other they lead to formation of an activated complex. It has highest energy among reactants, products and activated complex. When it decomposes to give product, energy is released and stability of product increases.

Since, the entire concentration of activated complex do not convert into products, while some activated complex may give reactants also.

20. (a, c, d)

The catalyst does not affect the value of equilibrium constant of the reaction.

Matching Column Type

21. (A→3), (B→1), (C→4), (D→6), (E→2), (F→5)

1. Catalyst alters the rate of reaction by lowering activation energy.
2. Molecularity can't be fraction or zero. If molecularity is zero, the reaction is not possible.
3. Second half-life of first order reaction is same as first because half-life time is temperature independent.
4. $e^{-E_a/RT}$ refers to the fraction of molecules with kinetic energy equal to or greater than activation energy.

5. Energetically favourable reactions are sometimes slow due to improper orientation of molecule cause some ineffective collision of molecules.
6. Area under the Maxwell, Boltzmann curve is constant because total probability of molecule taking part in a chemical reaction is equal to one.

Integer Type

22. (3) $\frac{r_2}{r_1} = (\mu)^{\Delta T/10}$

$$\frac{7.02\times10^{-2}}{2.6\times10^{-3}} = (\mu)^{30/10}$$

$\Rightarrow \quad 27 = \mu^3$

$\therefore \quad \mu = 3.$

23. (9) Heat of reaction = $E_f - E_b \Rightarrow -3 = 6 - E_b$
$E_b = 9$ kcal.

Comprehension Type

24. (c) $\log A = 14 \quad \therefore A = 10^{14}\ \text{sec}^{-1}$

25. (b) According to Arrhenius equation, $k = A\,e^{-E_a/RT}$
When $T = \infty$ K, $k = A$

26. (b) Given $\log_{10} k = 14 - \frac{1.25\times10^4\text{K}}{T}$ (i)

$$\log k = \log A - \frac{E_a}{2.303\ \text{RT}} \quad \text{(ii)}$$

Comparing equations (i) and (ii), we get

$$\frac{E_a}{2.303\ \text{R}} = 1.25\times10^4$$

$$E_a = 2.303\times1.987\times1.25\times10^4\ \text{cal mol}^{-1}$$

$$\approx 57.2\ \text{kcal mol}^{-1}$$

27. (a) $k = Ae^{-E_a/RT}$
Taking logarithm, we get

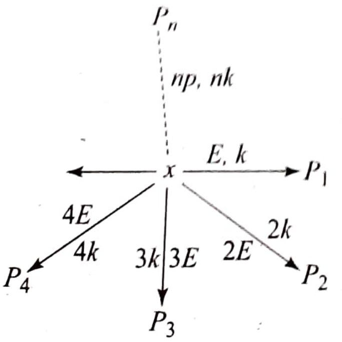
$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303\ \text{R}}\times\frac{1}{T}$$

$y = c + mx$
When $\log_{10} k$ is plotted against $1/T$ we get a straight line with intercept $\log_{10} A$.

DPP 4.6

Subjective Type

1. $E_{\text{dgy}} = E/3\,(2n+1)$



For n part disintegration we can apply.

$$E_{\text{overall}} = \frac{\sum_{n=1}^{i=n} k_i E_i}{k_i} = \frac{kE + 4kE + 9kE + 16kE + n^2kE}{k + 2k + 3k + \ldots}$$

$$= \frac{[1 + (2)^2 + (3)^2 + \ldots (n)^2]E}{1 + 2 + 3\ldots}$$

2. (a) $A \xrightarrow[K_1 = 45\ \text{hr}^{-1}]{K_1} B \xrightarrow[K_2 = 15\ \text{hr}^{-1}]{K_2} C$

$$t_{\max} = \left[\frac{\ln K_1 - \ln K_2}{K_1 - K_2}\right] = \frac{\ln\left(\frac{K_1}{K_2}\right)}{K_1K_2}$$

$$= \left(\frac{\ln 3}{30} = 3.67\times10^{-2}\ \text{hr} = 131.8\ \text{sec.}\right)$$

(b) $[B]_{\max} = [A]_0\left[\frac{K_2}{K_1}\right]^{\left(\frac{K_2}{K_1-K_2}\right)}$

$$= 1\times\left[\frac{15}{45}\right]^{\left(\frac{15}{45-15}\right)} = \left(\frac{1}{3}\right)^{1/2} = 0.58$$

(c) $[A]_t = ae^{-K_1t} = 1\times e^{-45\times60\times60} = 0$

3. ℓ – potassium chromo-oxalate $\rightleftharpoons$ d potassium chromo-oxalate
$t = 0 \qquad a \qquad 0$
$t = t_{\text{eq.}} \qquad (a - x_{\text{eq}}) \qquad x_{\text{eq}}$

$$K_{\text{eq.}} = \frac{K_f}{K_b} = \left(\frac{x_{\text{eq.}}}{a - x_{\text{eq}}}\right)$$

As $x_{\text{eq.}} = \frac{a}{2}; \quad K_f = K_b$

$$(K_f + K_b) = \frac{2.303}{t}\log\left(\frac{x_{eq.}}{x_{eq.} - x}\right)$$

$$2K_f = \frac{2.303}{560}\log\left(\frac{0.5a}{0.5a - 0.12a}\right)$$

$$2K_f = 5.42\times10^{-4}$$

$$K_f = K_b = 2.71\times10^{-4}$$

4. Volume of O_2 at any time $\propto$ mole of H_2O_2 decomposed
$\therefore \quad a \propto 35.75$

At $t = 10$, $\propto 6.30$

$$\therefore\ K = \frac{2.303}{10}\log_{10}\frac{35.75}{35.75 - 6.30} = 1.94\times10^{-2}$$

At $t = 15$, $x \propto 8.95$

$$K = \frac{2.303}{15}\log_{10}\frac{35.75}{35.75 - 8.95} = 1.92\times10^{-2}$$

At $t = 20$, $x \propto 11.40$

$$K = \frac{2.303}{20}\log_{10}\frac{35.75}{35.75 - 11.40} = 1.92\times10^{-2}$$

At $t = 25$, $x \propto 13.50$

$$K = \frac{2.303}{25}\log_{10}\frac{35.75}{35.75 - 13.50} = 1.90\times10^{-2}$$

Since, K values are constant using I order equation and thus, reaction obeys Ist order kinetics.

$K = 1.92 \times 10^{-2}$ minute^{-1}.

5. $\because$ Volume of alkali used $\propto$ Mole of acid at that time

$\therefore$ At $t = 0$, i.e., $V_0 \propto$ Mole of HCl

$\therefore$ At $t = 0$, i.e., $V_t \propto$ Mole of HCl + Mole of CH_3COOH formed at $t = t$

At $t = \infty$, i.e., $V_\infty \propto$ Mole of HCl + Total mole of CH_3COOH formed

$\therefore$ $a \propto V_\infty - V_0$ i.e., total ester

$(a - x) \propto V_\infty - V_0$ i.e., left ester at $t = t$

At $t = 75$,

$$K_1 = \frac{2.303}{75}\log_{10}\frac{42.03-19.24}{42.03-24.20} = 3.27\times10^{-3}\ \text{min}^{-1}$$

At $t = 119$,

$$K_2 = \frac{2.303}{119}\log_{10}\frac{42.03-19.24}{42.03-26.60} = 3.28\times10^{-3}\ \text{min}^{-1}$$

At $t = 259$,

$$K_{31} = \frac{2.303}{259}\log_{10}\frac{42.03-19.24}{42.03-32.23} = 3.26\times10^{-3}\ \text{min}^{-1}$$

Since, K values are constant and thus, reaction obeys Ist order kinetics.

Also, $K = \dfrac{K_1 + K_2 + K_3}{3} = 3.27 \times 10^{-3}\ \text{min}^{-1}$

6. At $t = 0$, Rotation $r_0 \propto$ Mole of sugar + rotation due to external factors

At $t = t$, Rotation $r_t \propto$ Left sugar + rotation due to external factors

At $t = \infty$, Rotation $r_\infty \propto$ External factors

$\therefore$ a = Mole of sugar $\propto r_0 - r_\infty$ at $t = 0$

$(a - x)$ = Left mole of sugar $\propto r_t - r_\infty$ at $t = t$

$$\therefore\quad K_1 = \frac{2.303}{30}\log_{10}\frac{46.75+18.75}{41+18.75} = 3.06\times10^{-3}\ \text{min}^{-1}$$

$$K_{31} = \frac{2.303}{90}\log_{10}\frac{46.75+18.75}{30.75+18.75} = 3.11\times10^{-3}\ \text{min}^{-1}$$

$$K_3 = \frac{2.303}{230}\log_{10}\frac{46.75+18.75}{12.75+18.75} = 3.18\times10^{-3}\ \text{min}^{-1}$$

Since, K values are constant and thus, reaction obeys Ist order kinetics.

Also, $K = 3.12 \times 10^{-3}$ min^{-1}.

Single Correct Answer Type

7. **(a)** $r_{10} = 50°, r_\infty = 100°, r_0 = 0$

$$\therefore k = \frac{2.303}{10}\log\left(\frac{100-0}{100-50}\right) = 0.0695\ \text{min}^{-1}$$

8. **(b)** $\dfrac{dC_R}{dt} = 0$

Differentiating

$$t_{\max} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$

9. **(b)** X will decrease

Y will increase then decrease

Z will increase

10. **(c)** Let $C_A = [A]$ at time t

And $C_{A0} = [A_0]$ at time $t = 0$

Then from Ist order eqn.

$$C_{A_0} = C_A \cdot e^{k_1 t}$$

or $\boxed{C_A = C_0 e^{-k_1 t}}$

11. **(b)** For parallel path reaction

$$k_{av} = k_1 + k_2$$
$$= 1.26 \times 10^{-4} + 3.8 \times 10^{-5}$$
$$= 1.64 \times 10^{-4}\ \text{s}^{-1}$$

$$\%\text{ of } B = \frac{k_1}{k_{av}} \times 100 = \frac{1.26\times10^{-4}}{1.64\times10^{-4}} = 100$$
$$= 76.83\%$$

$$\%\text{ of } C = \frac{k_2}{k_{av}} = \frac{3.8\times10^{-5}}{1.64\times10^{-4}} \times 100$$
$$= 23.17\%$$

12. **(b)** In given sequence of reaction $\dfrac{d[C]}{dt} = k_2[B] - k_3[C]$

13. **(c)** $RCOOR' + H_2O \xrightarrow{H^+} RCOOH + R'OH$

at $t = 0$:	a	0	0
at time t:	$(a - x)$	x	x
at time ∞:	$(a - a)$	a	a

at $t = 0$, V_0 = volume of NaOH due to H^+ (catalyst)

$$V_t = x + V_0$$
$$V_\infty = a + V_0$$

If ester is 50% hydrolysed, then $x = \dfrac{a}{2}$.

$$V_t = \frac{a}{2} + V_0$$

$$a = 2V_t - 2V_0$$

$$\therefore\quad V_\infty = 2V_t - 2V_0 + V_0 = 2V_t - V_0$$

14. **(a)** When 50% inversion has taken place then

$$(a - x) = \frac{a}{2}$$

$$2(a - x) = a$$
$$2(r_\infty - r_t) = r_\infty - r_0$$
$$2r_\infty - 2r_t = r_\infty - r_0$$
$$r_0 = 2r_t - r_\infty$$

15. **(c)** $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

1 : 1

It follows second order rate law

$$k = \frac{1}{t}\left[\frac{1}{a-x} - \frac{1}{a}\right]$$

At start 5 mL of NaOH ≡ 10 mL of 1 N HCl

$\therefore$ a = millimoles of NaOH at start = 10 × 1 = 10

After 10 min, $(a - x)$ = millimoles of NaOH = 8 × 1 = 8

$$\therefore\quad k = \frac{1}{10}\left[\frac{1}{8} - \frac{1}{10}\right]$$

Multiple Correct Answers Type

16. **(a, b, c)**

For the given curve

(a) $a = E_B$

(b) $b = E_A$

(c) $\Delta H_A = b - d$ and $\Delta H_B = a - c$

17. (b, c)

(a) It is a second order reaction. Its rate expression is rate = k [ester] [OH^-]

(d) A few reaction of order three are also known.

18. (b, d)

$$\text{Rate of reaction} = -\frac{1}{2}\frac{d[NO_2]}{dt} = k_1[NO_2]^2 = k_2[N_2O_4]$$

∴ Rate of disappearance of NO_2

$$= -\frac{d[NO_2]}{dt}$$

$$= 2k_1\,[NO_2]^2 - 2K_2\,[N_2O_4]$$

$$\text{or} \quad = 2k_1\,\{[NO_2]^2 - \frac{k_2}{k_1}[N_2O_4]\}$$

19. (a, c)

$$\frac{d}{dt}[NH_2CONH_2] = K_4[NH_3]\,[HNCO] \text{ from (iii)}$$

Applying steady state approximation to HNCO or NH_3

$$\frac{d[HNCO]}{dt} = 0 = K_3[NH_4NCO] - K_4[NH_4][HNCO]$$

$$\therefore \quad \frac{K_3}{K_4} = \frac{[NH_3][HNCO]}{[NH_3CNO]}$$

$$\frac{d_{[\text{urea}]}}{dt} = K_4 \times [NH_3][HNCO] = K_4 \times \frac{K_3}{K_4}[NH_4NCO]$$

$$\text{Also, } [NH_4NCO] = \frac{K_1}{K_2} \times [NH_4CNO]$$

$$\therefore \quad \frac{d_{[\text{urea}]}}{dt} = K_3 \times \frac{K_1}{K_2}[NH_4CNO] = K[NH_4CNO]$$

20. (a, b, c, d)

$$K_c = \frac{K_f}{K_b} = \frac{[C_6H_{12}]}{[C_6H_6][H_2]^3} = \frac{[C_6H_{12}]}{[C_6H_6][H_2][H_2]^2}$$

$r_f = K_f \times [C_6H_6][H_2]$

$r_b = K_b \times \text{Unknown}$

At eq. $r_f = r_b$

∴ $K_f[C_6H_6][H_2] = K_b \times \text{Unknown}$

$$\therefore \quad \text{Unknown} = \frac{K_f}{K_b} \times [C_6H_6][H_2]$$

$r_b = K_b \times \text{Unknown}$

$$r_b = K_b \times \frac{K_f}{K_b} \times [C_6H_6][H_2]$$

$= K_f \times [C_6H_6][H_2]$

$= K_b \times [C_6H_6][H_2]^{-2}.$

Matching Column Type

21. (a → s), (b → p, t), (c → q), (d → r)

Enzyme – catalyzed reactions:

$$\text{Substrate} \xrightarrow{\text{Enzyme}} \text{Product}$$

Rate = k[enzyme]^1 [substrate]^0

Since the concentration of the substrate is in excess and that of enzyme is small.

∴ Enzyme catalyzed reactions are zero order with respect to substrate.

Saponification of an ester is a second order reaction.

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

Acid hydrolysis of ester and of cane sugar are first order.

$$CH_3COOR'\,(\text{Ester}) + H_2O + HCl(H^{\oplus}) \longrightarrow CH_3COOH + C_2H_5OH$$

$$C_{12}H_{22}O_{11} + H_2O + H^{\oplus} \longrightarrow \underset{(\text{Glocose})}{C_6H_{12}O_6} + \underset{(\text{Fructose})}{C_6H_{12}O_6}$$

Integer Type

22. (4) $$E_{AV} = \frac{i=n\;k_iE_i}{\underset{n=1}{Z}\;k_i} = \frac{kE + 4kE + 9kE + 16kE + n^2kE}{k + 2k + 3k + \ldots}$$

$$= \frac{[1+(2)^2+(3)^2+\ldots(n)^2]E}{1+2+3\ldots}$$

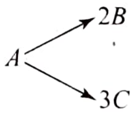
And $E_{AV} = 3E$

$$\therefore \text{ For } n = 4,\ E_{AV} = \frac{[1+(2)^2+(3)^2+(4)^2]E}{1+2+3+4} = 3E.$$

23. (3) $$\text{Average half life} = \frac{1}{t} = \frac{t_1\,t_2}{t_1+t_2} = \frac{4\times 12}{12+4} = \frac{48}{16} = 3$$

Comprehension Type

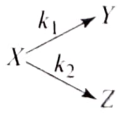
24. (c)



from stoichiometry

$$\therefore \quad [A]_0 = [A]_t + \frac{[B]_t}{2} + \frac{[C]_t}{3}$$

25. (b)



$$[X]_t = [X]_0\,e^{-\frac{(k_1+k_2)t}{k}} = [X_0]e^{-kt}$$

$$\therefore \quad \frac{[X]_t}{[Y_t][Z_t]} = \frac{[X_0]e^{-kt}}{[X_0]e^{-k_1t}[X_0]e^{-k_2t}}$$

$$= \frac{e^{-kt}}{e^{-k_1t} + e^{-k_2t}}$$

where $k = k_1 + k_2$

26. (a) $$\frac{[B]}{[C]} = \frac{3k_1}{4k_2}$$

CHAPTER 5

DPP 5.1

Subjective Type

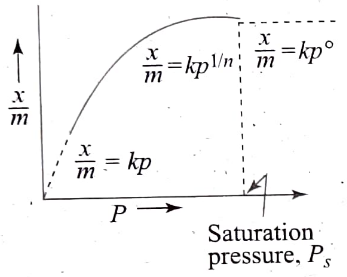
1. During adsorption, there is always a decrease in surface energy which appears as heat.

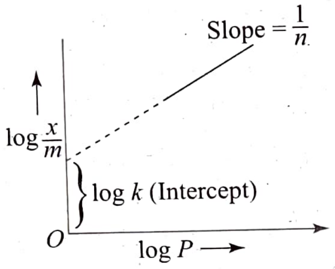
   ∴ ΔH of adsorption is always –ve.

   and ΔS (entropy of the gas) is also –ve.

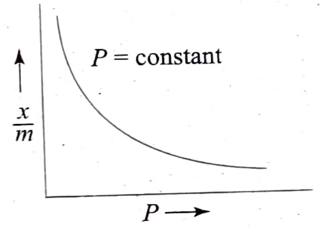
   and for a reaction to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, ΔG must be –ve.

2.

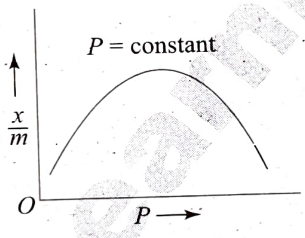




$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$



Physisorption Isobar



Chemisorption Isobar

3. Higher the critical temperature of a gas, greater the ease of liquefaction, i.e., greater the van der Waals' forces of attraction and hence greater the adsorption.

4. Freundlich Isotherm equation:-

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

At low pressure: $\frac{1}{n} = 1, \frac{x}{m} = kp$, i.e., $\frac{x}{m} \propto p$.

It follows first order kinetics.

At high pressure: $\frac{1}{n} = 0, \frac{x}{m} =$ const.

or $\frac{x}{m} = kp^{\circ}$ $\left(\because \frac{1}{n} = 0\right)$

It follows zero-order kinetics.

At intermediate range of pressure n lies between 0 and 1.

$$\frac{x}{m} = kp^{1/n}$$

Single Correct Answer Type

5. (c) The effect is called activated adsorption. Initially, the amount of gas adsorbed increases with rise in temperature. Further increase of temperature will increase the energy of molecules. This would decrease the extent of adsorption.

6. (c) Pressure of gas ∝ No. of gas molecules (mass) striking the given area of surface of adsorbent.

7. (c) The gas which is easily liquefied undergoes greater extent of adsorption on the surface of adsorbent. Thus, greater is the critical temperature, more is the extent of adsorption.

	H_2	N_2	CH_4	CO_2
T_C	33 K	126 K	190 K	304 K

Thus, CO_2 will be the most adsorbed gas on the surface of activated charcoal.

8. (b) Physical or van der Waals' adsorption is more pronounced at low temperature and high pressure.

9. (d) Graph A corresponds to monomolecular adsorption as postulated by Langmuir.

Graph C shows deviation from Langmuir model. The amount of adsorption keeps on rising with increase in pressure. This is attributed to the formation of additional layers of physically adsorbed gas molecules. For example, this graph is furnished by adsorption of nitrogen on an iron or a platinum catalyst at –195°C.

Graphs B and D have been observed in those cases in which there is possibility of condensation of gases in the minute capillary pores of the adsorbent at pressure even below the saturation pressure of the gas.

10. (d) In chromatography the separation is based on differential partitioning between the mobile and stationary phases. The various constituents of the mixture travel at different speeds, causing them to separate.

11. (c) When a diatomic gas adsorbs as atoms on the surface of a solid, the Langmuir adsorption isotherm becomes:

$$\theta = \frac{x}{m} = \frac{(kp)^{1/2}}{1 + (kp)^{1/2}}$$

12. (d) CH_3COOH adsorbed = 0.5 – 0.49 = 0.01 M

No. of molecules adsorbed

$$= 0.01 \times \frac{100}{1000} \times 6 \times 10^{23} = 6 \times 10^{20}$$

Total area of charcoal = $2 \times 3 \times 10^2$

$= 600\ m^2$

$$\Rightarrow \text{area per molecule} = \frac{600}{6 \times 10^{20}} = 1 \times 10^{-18}\ m^2$$

$= 1 \times 10^{-18} \times 10^4\ cm^2$

$= 1 \times 10^{-14}\ cm^2$

Multiple Correct Answers Type

13. (a, c, d)

Physical adsorption does not involve unimolecular layer. It is reversible in nature and it is favoured at low temperature. Degree of physical adsorption decreases with increase in temperature.

14. (a, d)
In case of solutions, in place of equilibrium pressure, we use equilibrium concentration. Of the adsorbents in the solution and the isotherms take the form

$$\frac{x}{m} = kc^{1/n}$$

Taking logarithm,

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log c$$

15. (a, b, c)
Chemisorption is stronger than physical adsorption and give rise to evolution of more heat.

16. (b, d)
Emulsifiers work on the principle of adsorption and adsorption is a surface phenomenon.

17. (a, b, d)
E_a is zero for physisorption and is positive for chemisorption.

Matching Column Type

18. (a → r), (b → p), (c → s), (d → q)

- The rate of absorption remains same throughout the process.
- In physisorption, enthalpy of adsorption is quite low (20 to 40 kJ mol^{-1}).
- Desorption is an endothermic process.
- Rate of adsorption decreases as pressure increases in chemical adsorption.

Integer Type

19.(4) $\log\frac{x}{m} = \log k + \frac{1}{n}\log p$

$= 0.602 + 1 \log 1 = 0.602$

$\therefore \frac{x}{m} = 4$

Comprehension Type

20. (d) $\log\frac{x}{m} = \log k + \frac{1}{n}\log p$

It is of the form $y = mx + c$.

Therefore, slope of the line will be $\frac{1}{n}$.

21. (a) At high pressure,

$1 + bp \approx bp$

$\frac{x}{m} = \frac{ap}{bp} = \frac{a}{b}$

22. (a) At high pressure,

$\frac{x}{m} = \frac{ap}{1+bp}$ (and $1 + bp \approx bp$)

$= \frac{ap}{bp} = \frac{a}{b}$

DPP 5.2

Subjective Type

1. Thomas Graham (1861) studied the rates of diffusion of solutions of different substances through parchment membrane and as a result of his experiments, he divided the substances into two classes (i) crystalloids and (ii) colloids.

The non-diffusibility of colloids and diffusibility of crystalloids through the animal or vegetable membrane was shown to be due to the difference in the size of particles of crystalloids and colloids. The colloids form bigger particles which cannot pass through the membrane. It is, therefore, preferable to speak of a substance in "colloidal state" rather than calling it a crystalloid or a colloid.

Thus, we can say,

Colloidal state of matter is, therefore, a state in which the size of the particles is such that they can pass through filter paper but not through animal or vegetable membrane.

2. **(a)** Trace of electrolyte which stabilises the colloids is removed completely making the colloid unstable, so coagulation occurs on prolonged dialysis.

(b) A crystalloid was found to behave as a colloid under different set of conditions and vice versa. For example, sodium chloride behaves as a crystalloid when dissolved in water but behaves as a colloid when dissolved in benzene.

3. Colloidion is a 4% solution of nitrocellulose in a mixture of alcohol and ether.

Function:

Colloidion solution is used to stop the flow of colloidal particles through filter paper by reducing the size of pores of filter paper.

4. In case of Lyophilic sols, if the dispersion medium is separated from the dispersed phase, the sol can be reconstituted by simply remixing with the dispersion medium. That's why these sols are also called reversible sols.

But in case of Lyophobic sols, once they are precipitated, they do not give back the colloidal sol by simple addition of the dispersion medium. Hence, they are also called irreversible sols.

Single Correct Answer Type

5. (a) Purple of cassius is Au sol in water. It is used to raise vitality of human system.

6. (a) Black diamond is an impure form of polycrystalline diamond consisting of diamond, graphite and amorphous carbon.

7. (d) Sodium is a highly reactive metal. It reacts exothermally with water, to the point that sufficiently large pieces melt to a sphere and may explode.

8. (d) The colloidal system constituting the liquid as the dispersed phase and the solid as the dispersion medium is known as gel.

9. (d) Sol particles possess the tendency to adsorb preferentially the common ion present in solution.

10. (b) Colloidal state involves dispersion state, an intermediate state in between true solution and suspension state.

11. (d) Colloidal state possesses lower surface tension or increase in surface area. This provides sol to acquire peculiar properties e.g., more adsorption power.

Multiple Correct Answers Type

12. (b, c, d)
At CMC, ions aggregate to form micelles and thereby surface tension of solution is lowered.

13. (a, b)
Colloidal gold can be prepared by Bredig's arc method and by reduction of $AuCl_3$.

$$2AuCl_3 + 3SnCl_2 \longrightarrow 2Au \text{ (Gold sol)} + 3SnCl_4$$

14. (a, b, d)
Gel is a colloidal solution of liquid in solid.

15. (b, c)
Mechanical disintegration method is not suitable when the dispersion medium is an organic liquid as considerable charring occur and is used to prepare colloidal graphite and printing ink.

16. (a, b, c)
Gold is lyophobic in nature.

Matching Column Type

17. (a → r, s), (b → r, s), (c → p), (d → q)

D. Phase	D. Medium	Type of colloids	Example
Solid/Liquid	Gas	Aerosol	Mist, rain cloud
Gas	Liquid	Foam	Whipped cream
Liquid	Solid	Gel	Jellies

Comprehension Type

18. (b) Micelles are formed by association of surfactant molecule.

19. (c) Micelles are generally formed by the aggregation of several ions or molecular with lyophilic as well as lyophobic parts. Surfactants may act as detergents, emulsifiers and dispersants.

20. (c) The formation of micelles takes place only above a particular temperature called Kraft Temperature (T_k) and above a particular concentration called CMC.

21. (b, c)
Both aggregation and micelle formation takes place above CMC.

22. (a, c)
The cleansing action of soap is due to the fact that soap molecules form micelles around the oil droplet.

The terms micro emulsion and micellar solution are used to describe concentrated, surfactant-stabilized dispersions of water and hydrocarbons that are used to enhance petroleum recovery.

DPP 5.3

Subjective Type

1. Minimum quantity of an electrolyte required to cause precipitation of a sol is called its coagulating value. Greater the charge on flocculating ion and smaller is the amount of electrolyte required for precipitation, higher is the coagulating power of coagulating ion (Hardy-Schulze Law).

   Phosphate ion bear –3 charge while chloride ion carries only –1 charge and due to high charge phosphate ion has high coagulating power than that of chloride ion.

2. Emulsifying agent is added to emulsion to stabilise the emulsion. Emulsifying agent form a layer between suspended particles and the medium and hence stabilises the emulsion. Ice cream (emulsion) is stabilised by emulsifying agent like gelatin.
3. It can be identified by dilution test. In this method, the emulsion is diluted with water. If the emulsion gets diluted with water, this means that water acts as the dispersion medium and it is an example of oil-in-water emulsion. If it is not diluted, then oil acts as the dispersion medium and it is an example of water-in-oil emulsion.
4. Some amount of the electrolytes is mixed to form the precipitate remain adsorbed on the surface of the particles of the precipitate. Hence, it is essential to wash the precipitate with water to remove the sticking electrolyte or any other impurities before estimating it quantitatively.

Single Correct Answer Type

5. (b) $[AgI]I^{\ominus}$ colloid will be formed only when the iodide ion is present in excess.

6. (c) The dispersed phase particles bear continuous collisions with dispersion medium to show irregular motion in sol state.

7. (a) Lower is the value of gold number, more is its protecting power.

8. (b) Blood is –vely charged emulsion.

9. (b) The sol particles at isoelectric point do not show electrophoresis.

10. (d) Charge of $[Fe(CN)_6]^{4-}$ is highest hence it will be most effective for the coagulation of positive colloids.

11. (a) Smaller is size of particle, faster is motion.

12. (b) Number of milligrams of protective colloid added in 10 mL of colloidal gold to prevent its coagulation on addition of 1 mL of 10% NaCl solution is called gold number.

∴ Gold number of present colloidal substance = 25 (Gold number is usually given in mg.)

Multiple Correct Answers Type

13. (b, d)
Presence of equal and similar charges on colloidal particles provides stability to colloids as repulsive forces between charge particles having same charge prevent them from colliding when they come closer to each other.

14. (a, d)
The droplets present in emulsion have negative charge. It can be precipitated by adding electrolyte such as KCl, NaCl etc. Since, glucose and urea do not produce ions on dissolving in water. Hence, they are non-electrolyte and do not precipitate the negatively charged emulsion.

15. (a, b, d)
Maxwell distribution is for describing particle speeds in idealized gases where the particles move freely inside a stationary container.

16. (a, b)
High-voltage electricity is often an effective means of breaking emulsions. It is generally theorized that water droplets have an associated net charge, and when an electric field is applied, the droplets move about rapidly and collide with each other and coalesce. Other methods of demulsification are done by heating or freezing.

17. (a, c, d)

A protective colloid is a colloidal substance that protects other colloids from getting coagulated in the presence of an electrolyte colloidal silica is not a protective colloid.

Matching Column Type

18. (a → q), (b → s), (c → r), (d → p)

- Precipitation of colloidal sol is called coagulation.
- The process of separating the particles of colloids from those of crystalloids by diffusion of the mixture through an animal membrane is called dialysis.
- To compare the protective action of different lyophilic colloids, Gold number was given.

Comprehension Type

19. (a) As_2S_3 is a negative colloid hence Al^{3+} will be most effective for its coagulation.

20. (b) Greater is the charge of ion, more effective is the coagulation of oppositely charged colloid.

21. (d) Flocculating value of ion depends on both, the nature and magnitude of the charge of the flocculating ion.

22. (d) $[AgI]Ag^+$ will not be coagulated by the addition of Ag^+ or NO_3^- ions.

DPP 5.4

Subjective Type

1. Desorption is important for a substance to act as a good catalyst so that after the reaction, the products formed on the surface separate out (desorbed) to create free surface again for other reactant molecules to approach the surface and react.

   If desorption does not occur, then other reactants are left with no space on the catalysis surface for adsorption and reaction will stop.
2. Diffusion of gas molecules occur at the surface of catalyst (solid) followed by adsorption. In the same way, the product formed diffuse from the surface of the catalyst leaving the surface free for more reactant molecules to get adsorbed and undergo reaction.
3. When gaseous molecules come in contact with the surface of a solid catalyst, a weak chemical bond is formed between the surface (catalyst) molecules and reactant (gas) molecules. Thus, concentration of reactant molecules increases at the surface.

   The rate of reaction increases by adsorption of different molecules side by side facilitating the chemical reaction. Adsorption, being exothermic also help in increasing the rate of reaction (chemisorption increases with rise in temperature).
4. The catalytic reaction which depends upon pore structure of catalyst and the size of the reactant and product molecules is known as shape selective catalysts. Zeolites are good shape selective catalyst because of honey comb like structure.
   (i) They are microporous aluminosilicates with Al—O—Si framework and general formula $M_{x/n}\,[(AlO_2)_x\,(SiO_2)_y]\cdot mH_2O$
   (ii) The reactions taking place in zeolites depend upon the size and shape of the reactant and product molecules as well as upon the pores and cavities of the zeolites.
   (iii) Zeolites are widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerization. They are also used for removing permanent hardness of water.
   (iv) e.g., ZSM-5 is a catalyst used in petroleum industry.

$$\text{Alcohols} \xrightarrow[\text{Dehydration}]{\text{ZSM-5}} \text{Gasoline (petrol)}$$

(A mixture of hydrocarbons)

Single Correct Answer Type

5. (c) Homogeneous catalysis does not occur at the interface of phases as in case of homogeneous catalysis reactant and catalyst have same phase and their distribution is uniform throughout.

6. (a) (i) Reaction in which catalyst is in different phase than other (reactants and products) is known as heterogeneous catalysis.

(ii) $2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$

Here, reactant SO_2 and product SO_3 are in gaseous phase while platinum is in solid phase. So, this reaction represents a heterogeneous catalysis.

(iii) $N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$

Similarly, here N_2 and H_2 reactant are in gaseous phase while NH_3 is in solid phase. Whereas in other reactions catalyst is in same phase with reactant(s) and product(s).

7. (a) This is a fact.

8. (d) All are examples of negative catalysts.

9. (b) Enzymes decrease the activation energy to greater extent.

10. (c) Such a process involving oxidation of one substance in presence of other which would otherwise not been possible is called induced catalysis or better to say induced oxidation.

11. (a) ZSM-5 acts as an effective catalyst to convert alcohol to alkanes (petrol).

12. (b) In absence of catalyst: Activation energy $(E_a) = z$

In presence of catalyst: Activation energy $(E_a') = p$

$\therefore$ decrease in energy of activation $= E_a - E_a' = z - p$

Multiple Correct Answers Type

13. (a, b)

(a) Same reactants may give different products by using different catalysts as different catalysts have different specific functions to mold the reaction towards specific product. e.g., starting with H_2 and CO, and using different catalysts, we get different products.

(i) $CO(g) + 3H_2 \xrightarrow{Ni} CH_4(g) + H_2O(g)$

(ii) $CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO} CH_3OH(g)$

(iii) $CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$

(b) Catalyst does not change ΔH of reaction as ΔH of reaction is difference between enthalpy of reactants and products. So, it does not change during catalysed reaction.

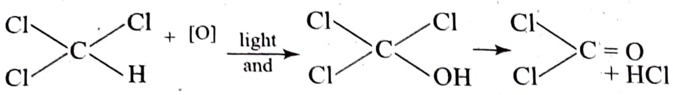
14. (a, b)

In a reaction, catalyst changes physically and qualitatively as it is unaltered during the reaction and remain quantitatively intact after completion of reaction and chemically does not change.

15. (a, b, c)

- An antiknock agent is a gasoline additive used to reduce engine knocking and increase the fuel's octane rating by raising the temperature and pressure at which auto-ignition occurs. Tetraethyl lead is still in use as a high octane additive.

- H_2O_2 decomposes to H_2O and O_2 in presence of light. That's why it is stored in dark glass bottles for this reaction. The inhibitors used are oxalic acid, urea or glycerol.



(Phosgene)
Highly poisonous

To convert phosgene to ethyl carbonate and to retard the oxidation 1% ethyl alcohol is used.

$$COCl_2 + C_2H_5OH \longrightarrow (C_2H_5)_2\,CO + 2HCl$$

16. **(b, c, d)**
Nickel is used as a catalyst in the hydrogenation of oils.

17. **(b, c, d)**
Catalyst provides an entirely new path for the reaction in which a newly activated intermediate complex of lower potential energy is formed.

Matching Column Type

18. **(a → s), (b → p), (c → q, r), (d → q)**

- Acetamide acts as a negative catalyst for the decomposition of H_2O_2.
- Zeolites are shape selective catalysts and used in removal of hardness of water.
- Nickel is a catalyst used in hydrogenation of oil.

Comprehension Type

19. **(c)** Decomposition of H_2O_2 is inhibited by acetamide.

20. **(c)** Amount of product, heat of reaction and equilibrium constants are unaltered by catalyst.

21. **(b)** Autocatalysis by Mn^{2+} is responsible for the faster oxidation.

22. **(a)** During a chemical reaction if one of the products form acts as a catalyst, the phenomenon is called auto catalysis.

CHAPTER 6

DPP 6.1

Subjective Type

1. Radioactive change is

$${}^{238}_{92}\text{U} \rightarrow {}^{206}_{82}\text{Pb}$$

Decrease in mass = (238 – 206) = 32
Let the number of α-particles emitted be x.

$$4x = 32$$
$$x = 8.$$

Thus, 8 moles of helium are produced when one mole of ${}^{238}_{92}\text{U}$ disintegrates into ${}^{206}_{82}\text{Pb}$.

2. $${}^{238}_{92}\text{U} - {}^{4}_{2}\text{He} \rightarrow {}^{234}_{90}\text{U}_{\text{X}_1}$$
$${}^{234}_{90}\text{U}_{\text{X}_1} - ({}^{0}_{-1}\text{e}) \rightarrow {}^{234}_{91}\text{U}_{\text{X}_2}$$

Both U_{X_1} and U_{X_2} will belong to IIIrd group because both lie in actinide series.

3. (a) Beta emission, (b) Alpha emission, positron emission capture, (c) Electron capture. (The capture of a K-shell electron leaves a vacancy, which is filled by a higher-energy electron. This transfer is accompanied by x-rays emission.)

4. (i) The nuclides near the "belt of stability" are probably stable; those above that belt are beta emitters; those below are positron emitters. Thus the stable nuclides are ^{208}Pb and ^{120}Sn; the beta emitters are ^{49}Ca, ^{30}Al and ^{94}Kr; the positron emitters are ^{195}Hg, ^{8}B and ^{150}Ho.
   (ii) ${}^{114}_{49}\text{In}$, which has an odd number of protons and an odd number of neutrons.

Single Correct Answer Type

5. (d) Antiproton has a negative charge.

6. (a) One Becquerel of radioactivity is equal to one integration per second.

7. (c) No. of α-particles $= \left(\dfrac{a-b}{4}\right)$

$$Z_1 - 2\alpha + \beta = Z_2$$
$$\beta = Z_2 - Z_1 + 2\alpha$$
$$= d - c + 2\frac{(a-b)}{4}$$
$$= d + \frac{(a-b)}{2} - c.$$

8. (b) After α, β-emission, nucleus goes to excited state. When it returns to normal state, emission of γ-radiations takes place.

9. (b) ${}^{A}_{Z}\text{X} - {}^{0}_{-1}e \rightarrow {}^{A}_{Z+1}\text{Y};\ {}^{A}_{Z+1}\text{Y} - {}^{4}_{2}\text{He} \rightarrow {}^{A-4}_{Z-1}\text{Z};\ {}^{A-4}_{Z-1}\text{Z} - \gamma \rightarrow {}^{A-4}_{Z-1}\text{Z}^*$

10. (c) Isodiapheres are formed by α-emission.

$${}^{235}_{92}\text{U} - {}^{4}_{2}\text{He} \rightarrow {}^{231}_{90}\text{Th} \text{ (Isodiaphere)}$$

11. (b) ${}^{A}_{Z}\text{X} \rightarrow {}^{A-8}_{Z-3}\text{Y}$

$$\text{Number of } \alpha\text{-particles} = \frac{\text{Change in mass number}}{4} = \frac{8}{4} = 2$$

Z – 2 × Number of α-particles + Number of α- and β-particles = Z – 3
Z – 2 × 2 + Number of β-particles = Z – 3
Number of β-particles = 1.

Multiple Correct Answers Type

12. **(b, c)**
A is ${}^{234}_{90}\text{Th}$ which belongs to III B group
B is ${}^{230}_{88}\text{Ra}$ and belongs to II A group.

13. **(c, d)**
γ-decay is secondary effect of α, β-decay; it does not alter electrically neutral.
In K-electron capture, electron and proton combine as follows.

$${}^{0}_{-1}e + {}^{1}_{1}\text{H} \rightarrow {}^{1}_{0}n$$

Thus, electrical neutrality of atom remains unchanged.

14. **(a, b, d)**
Isodiapheres have same isotopic excess mass i.e., neutron – protons.
Example: ${}^{235}_{92}\text{U} \xrightarrow{-\alpha} {}^{231}_{90}\text{Th}$.

15. **(b, c, d)**
Nuclear isomerism : The relation of two or more nuclides that have the same atomic number and mass number but different energy levels and half-lives.

16. **(a, c, d)**
A and B are isodiapheres, and A and C are also isodiapheres.

Matching Column Type

17. **(a → p, r); (b → s); (c → q); (d → r)**
During α-emission mass number decreases by four units and atomic number decreases by two units
During β-emission mass number does not change but atomic number increases by one unit
During γ-emission atomic number and mass number remain unchanged
During β^{+}-emission mass number does not change but atomic number decreases by one unit.

Integer Type

18. (6) ${}^{234}_{90}\text{Th} \rightarrow {}^{206}_{82}\text{Pb}$
Parent End product

Decrease in mass = (234 – 206) = 28

Mass of α-particles = 4

So, Number of α-particles emitted $= \frac{28}{4} = 7$

No. of β-particles emitted = 2 × No. of α-particles – (At. No. of parent – At. No. of end product)

$= 2 \times 7 - (90 - 82) = 6.$

19. (5) The decrease in atomic mass = (232 – 212) = 20

Decrease in mass occurs due to emission of α-particles. Let x be the number of alpha particles emitted.

Mass of 'x' α-particles = $4x$

So, $4x = 20$

or $x = \frac{20}{4} = 5$

Comprehension Type

20. (b) $^{230}_{88}\text{Ra}$ belongs to alkaline earth family.

21. (b) $^{232}_{90}\text{Th} \rightarrow {}^{208}_{82}\text{Pb} + \sigma\, {}^{4}_{2}\text{He} + 4\text{e}^{0}_{-1}$

22. (b) Excess electrons are lost due to exchange of electron with atmosphere. Radioactive decay leads to neutral atom.

23. (b) γ-rays are given by unstable nuclide left after α, β-emissions and are known as secondary emission.

DPP 6.2

Subjective Type

1. (a) In this nuclear reaction, since the mass of electron is included in Ca atom, we have

Δm = Atomic mass of (Ca – K) = (39.962589 – 39.964008) amu = -1.419×10^{-3} amu

$E = -1.419 \times 10^{-3} \times 931$ MeV = –1.32 MeV

(b) In this nuclear reaction, since the mass of electron is included in K atom, we have

Δm = Atomic mass of (Ar – K) = (39.962348 – 39.964008) amu = -1.624×10^{-3} amu

$E = -1.624 \times 10^{-3} \times 931$ MeV = –1.51 MeV

(c) In this nuclear reaction, there is a loss of 2 electronic masses from K atom. Hence,

Δm = Atomic mass of (Ar – K) + mass of 2 electrons

= (39.962384 – 39.964008 + 2 × 0.0005486) amu

$= -5.27 \times 10^{-4}$ amu

Hence, $E = -5.27 \times 10^{-4} \times 931$ MeV = –0.49 MeV.

2. Difference = m(U atom) – m(He atom) – m(Th atom)

$= [m(\text{U nucleus}) + 92m_e] - [m(\text{He nucleus}) + 2m_e]$

$- [m(\text{Th nucleus}) + 90m_e]$

$= m(\text{U nucleus}) - m(\text{He nucleus}) - m(\text{Th nucleus})$

(There is a very small difference, due to electronic binding energies, between the rest mass of a neutral atom and the sum of the nuclear and electronic rest masses.)

3. The process referred to is $^{6}_{2}\text{He} \rightarrow {}^{6}_{3}\text{Li} + \beta^-$. In computing the mass change during this process, only the whole atomic masses of ^{6}He and ^{6}Li need be considered.

Mass of ^{6}He = 6.01889 u Mass of ^{6}Li = 6.01512 u

Loss in mass = 0.00377 u

Energy equivalent = (932)(0.00377) MeV = 3.51 MeV

The maximum kinetic energy of the β^- particle is 3.51 MeV.

4. ^{7}Be has a larger mass than ^{7}Li. Thus $^{7}_{4}$Be can decay spontaneously into $^{7}_{3}$Li, but not vice versa. There are two types of decay process in which Z is decreased by one unit without a change in mass number A : β^+ emission and K capture. These two processes have different mass balance requirements.

Assume that the process is β^+ emission. $^{7}_{4}\text{Be} \rightarrow \beta^+ + {}^{7}_{3}\text{Li}$

Mass difference = [M(nucleus) for ^{13}N] – [M(nucleus) for ^{13}C] – M(e)

That a positron emission occurs (i.e., Q is positive and the reaction is spontaneous) only if the nucliedic mass of the parent species exceeds the nucliedic mass of the daughter by at least twice the rest mass of the electron, 2(0.00055) = 0.00110 u. In the present case, the actual mass difference between parent and daughter nuclides 7.01600 = 0.00093 u. We thus see that positron emission in this case is impossible. By elimination, we conclude that ^{7}Be undergoes K capture.

Single Correct Answer Type

5. (a) Binding energy per nucleon (8.8 MeV) is maximum for nucleus with mass number 56 i.e., for iron.

6. (a) Binding energy = (0.10242 amu) $\left(\frac{931 \text{ MeV}}{1 \text{ amu}}\right)$ = 95.35 MeV.

7. (c) Change in charge number = 6(–2) + 4(+1) = –8. Change in mass number = 6(–4) = –24.

8. (c) The element with highest binding energy per nucleon is most stable.

9. (c) Total binding energy of ^{17}O = (17)(7.75 MeV) = 131.75 MeV

Total binding energy of ^{16}O = (16)(7.97 MeV) = 127.52 MeV

Energy required to remove a neutron from ^{17}O = (131.75 – 127.52) MeV = 4.23 MeV

10. (b) $4n + 1$ series involves $^{241}_{94}\text{Pu} \xrightarrow[5\beta \text{ particles}]{8\alpha \text{ particles}} {}^{209}_{83}\text{Bi}.$

11. (c) W → 2Y

Binding energy of W = 7.5 × 120 = 900 MeV

Binding energy of 2Y = 2(8.5 × 60) = 1020 MeV

Binding energy (2Y) > Binding energy of (W).

Thus, energy will be released.

Multiple Correct Answers Type

12. (a, d)

These elements belong to ($4n$ + 3) series.

13. (c, d)

$4n$ + 1 series	$^{232}_{90}\text{Th} \rightarrow {}^{208}_{82}\text{Th};$	6 alpha and four beta
4n + 2 series	$^{238}_{92}\text{U} \rightarrow {}^{206}_{82}\text{Pb};$	8 alpha and six beta
4n + 3 series	$^{239}_{92}\text{U} \rightarrow {}^{207}_{82}\text{Pb};$	8 alpha and six beta

14. (a, c)

Nuclei with mass number around 60 have the highest binding energy per nucleon and species of mass number 4, 12 and 16 have high binding energy per nucleon.

15. (a, b, c)

Δm = atomic mass of $({}_4\text{Be}^8 - {}_5\text{B}^8)$ + mass of one electron

16. (b, c)

$E = mc^2$, where m = mass defect

c = velocity of light = 3×10^{10} cm s^{-1}

$\therefore \quad E = 1.66 \times 10^{-24} \times (3 \times 10^{10})^2$

$= 14.94 \times 10^{-4}$ erg $= 1.494 \times 10^{-10}$ J

(1 MeV = 1.602×10^{-13} J)

$$\therefore \quad E = \frac{1.494 \times 10^{-10}}{1.602 \times 10^{-13}} = 931.5 \text{ MeV}.$$

Matching Column Type

17. (a → p, q); (b → r, q); (c → p, r); (d → s)

$${}^{234}_{90}\text{Th} \xrightarrow{7\alpha,\ 6\beta} {}^{206}_{82}\text{Pb}; \quad {}^{235}_{92}\text{U} \xrightarrow{(7\alpha,\ 6\beta)} {}^{221}_{84}\text{Po};$$

$${}^{238}_{92}\text{U} \xrightarrow{(8\alpha,\ 6\beta)} {}^{206}_{82}\text{Pb}; \quad {}^{232}_{90}\text{Th} \xrightarrow{(6\alpha,\ 4\beta)} {}^{208}_{82}\text{Pb};$$

$$\text{Number of } \alpha\text{-particles } (x) = \frac{\text{Change in number}}{4} = \frac{(M_1 - M_2)}{4}$$

Let y, β-particles are evolved in the decay then $Z_1 - 2x + y = Z_2$, Where Z_1 and Z_2 are initial and final atomic number.

Integer Type

18. (8) The nucleus of ${}^{56}_{26}\text{Fe}$ contains 26 protons and 30 neutrons. Hence,

Mass of 26 protons = 26 × 1.00737 amu = 26.19162 amu

Mass of 30 neutrons = 30 × 1.00866 amu = 30.2598 amu

Total mass of 26 protons and 30 neutrons = (26.19162 + 30.25980) amu = 56.45142 amu

Mass defect = (56.45142 – 55.9615) amu = 0.48986 amu

Binding energy = 0.48986 × 931 MeV = 456.064 MeV

$$\text{Binding energy per nucleon} = \frac{456.064 \text{ MeV}}{56} = 8.143 \text{ MeV}.$$

19. (9)

$$\text{B.E./nucleon} = \frac{\text{Total B.E.}}{\text{No. of nucleons}}.$$

$$\text{No. of nucleons} = \frac{63}{7} = 9$$

Comprehension Type

20. (c) Mass decay = $N \cdot M_n + Z \cdot M_p - M(N, Z)$

B. E. = Mass decay × C^2

$$\therefore \text{Mass decay} = \frac{B}{C^2}$$

$$\frac{B}{C^2} = NM_n + ZM_p - M(N, Z)$$

$$\therefore \quad M(N, Z) = NM_n + ZM_p - \frac{B}{C^2}.$$

21. (c) Mass decay = (mass of ${}^4_2\text{He}$ + mass of ${}^1_0n$) – (mass of ${}^2_1\text{H}$ + mass of ${}^3_1\text{H}$) $(\because \Delta m = E \times u^2)$

$$= \frac{\text{B.E. of } {}^4_2\text{He} + 0 - \text{B.E. of } {}^2_1\text{H} - \text{B.E. of } {}^3_1\text{H}}{u^2}$$

$$\text{Mass decay} = \frac{c - a - b}{u^2}$$

$$\text{Now, } E = \text{mass decay} \times u^2 = \frac{c - a - b}{u^2} \times u^2 = c - a - b$$

22. (b) ${}_6\text{C}^{14} \rightarrow {}_7\text{N}^{14} + {}_{-1}e^0$

$\Delta m = 14.00324 - 14.00307 = 0.00017$ amu

$\therefore$ Energy produced during this decay of 1 atom

$= \Delta m \times 931.478$ MeV

$= 0.00017 \times 931.478$ MeV

$= 0.158$ MeV

$= 0.158 \times 10^6$ eV

$= 0.158 \times 10^6 \times 1.602 \times 10^{-19}$ J

$= 2.53 \times 10^{-14}$ J

Now, 1 curie of C^{14} means decay of 3.70×10^{10} dps.

Thus, energy produced during decay of 1 curie mass of C^{14}

$= 3.70 \times 10^{10} \times 2.53 \times 10^{-14}$ J s^{-1}

$= 9.36 \times 10^{-4}$ J

$\therefore$ Energy produced during 1 hr

$= 9.36 \times 10^{-4} \times 60 \times 60 = 3.37$ J

DPP 6.3

Subjective Type

1. We have

$$\frac{\text{Number of tritium (T) atoms}}{\text{Number of hydrogen (H) atoms}} = \frac{8.0 \times 10^{-18}}{1}$$

$$\text{or} \quad \frac{\text{Number of } (\text{T}_2\text{O}) \text{ molecular}}{\text{Number of } \text{H}_2\text{O} \text{ molecular}} = \frac{8.0 \times 10^{-18}/2}{1/2} = \frac{8.0 \times 10^{-18}}{1}$$

$$\text{or} \quad \frac{\text{Amount of } (\text{T}_2\text{O}) \text{ molecular}}{\text{Amount of } \text{H}_2\text{O} \text{ molecular}} = \frac{8.0 \times 10^{-18}/6.023 \times 10^{23}}{1/6.023 \times 10^{23}} = \frac{8.0 \times 10^{-18}}{1}$$

$$\text{or} \quad \frac{\text{Mass of } (\text{T}_2\text{O}) \text{ molecular}}{\text{Mass of } \text{H}_2\text{O} \text{ molecular}} = \frac{22 \times 8 \times 10^{-18}}{18}$$

Mass of T_2O molecules in 10.0 of sample of water

$$= \frac{22 \times 8 \times 10^{-18}}{18 + 22 \times 8 \times 10^{-18}} \times 10.0 \text{ g}$$

$$= \frac{22 \times 8 \times 10^{-18}}{18} \times 10.0 \text{ g} = 9.777 \times 10^{-17} \text{ g}$$

$$\text{Amount of } \text{T}_2\text{O} \text{ molecules} = \frac{9.777 \times 10^{-17} \text{ g}}{22 \text{ g mol}^{-1}} = 4.444 \times 10^{-16} \text{ mol}$$

Now using the integrated rate expression $\log \dfrac{[\text{T}_2\text{O}]}{[\text{T}_2\text{O}]_0} = -\dfrac{k}{2.303} t$

For the first order reaction, we get

$$\log n(\mathrm{T_2O}) = \log n_0(\mathrm{T_2O}) - \frac{1}{2.303}\left(\frac{0.693}{t_{0.5}}\right)t$$

$$= \log(4.444\times10^{-16}) - \frac{1}{2.303}\left(\frac{0.693}{12.2\ y}\right)(40\ y)$$

$$= -15.3522 - 0.9786 = -16.3308$$

or $n(\mathrm{T_2O}) = 4.6687\times10^{-17}$ mol

Number of $\mathrm{T_2O}$ molecules $= (4.6687\times10^{-17})(6.023\times10^{23})$
$= 2.812\times10^{7}$

Number of T atoms $= 2\times2.812\times10^{7} = 5.624\times10^{7}$.

2. The nuclear reactions are as follows:

β^- emission $^{64}_{29}\mathrm{Cu} \rightarrow {}^{64}_{30}\mathrm{Zn} + {}^{0}_{-1}e$ β^+emission $^{64}_{29}\mathrm{Cu} \rightarrow {}^{64}_{28}\mathrm{Ni} + {}^{0}_{+1}e$

Electron capture $^{64}_{29}\mathrm{Cu} + {}^{0}_{-1}e \rightarrow {}^{64}_{82}\mathrm{Ni}$

If r_1, r_2 and r_3 are the respective rates of decay of Cu and r is the overall rate of decay of Cu, we will have $r = r_1 + r_2 + r_3$ i.e., $\lambda[\mathrm{Cu}] = \lambda_1[\mathrm{Cu}] + \lambda_2[\mathrm{Cu}] + \lambda_3[\mathrm{Cu}]$
i.e., $\lambda = \lambda_1 + \lambda_2 + \lambda_3$ (1)

The overall decay constant λ is given by

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{12.8\ \mathrm{h}} = 5.414\times10^{-2}\ \mathrm{h^{-1}} \quad (2)$$

It is given that $\frac{\lambda_1}{\lambda_2} = \frac{38}{43} = 0.884$ and $\frac{\lambda_2}{\lambda_3} = \frac{19}{43} = 0.442$

Substituting these in Eq. (1), we get $\lambda = 0.884\,\lambda_3 + 0.442\lambda_3 + \lambda_3$
$= 2.326\lambda_3$

Hence,

$$\lambda_3 = \frac{\lambda}{2.326} = \frac{5.414\times10^{-2}\ \mathrm{h^{-1}}}{2.326} = 2.328\times10^{-2}\ \mathrm{h^{-1}};$$

$$(t_{1/2})_3 = \frac{0.693}{\lambda_3} = \frac{0.693}{2.328\times10^{-2}\ \mathrm{h^{-1}}} = 29.77\ \mathrm{h}$$

$$\lambda_1 = 0.884\,\lambda_3 = (0.884)(2.328\times10^{-1}\,\mathrm{h^{-1}}) = 2.058\times10^{-2}\ \mathrm{h^{-1}}$$

$$(t_{1/2})_1 = \frac{0.693}{\lambda_1} = \frac{0.693}{2.058\times10^{-2}\ \mathrm{h^{-1}}} = 33.67\ \mathrm{h}$$

$$\lambda_2 = 0.442\,\lambda_3 = (0.442)(2.328\times10^{-2}\ \mathrm{h^{-1}}) = 1.029\times10^{-2}\ \mathrm{h^{-1}}$$

$$(t_{1/2})_2 = \frac{0.693}{\lambda_2} = \frac{0.693}{1.029\times10^{-2}\ \mathrm{h^{-1}}} = 67.35\ \mathrm{h}$$

3. (a) $A_0 = \lambda N_0 = 0.500\ \mathrm{mCi}\ \dfrac{0.963}{19.9\times365\times24.0\times3600}$

$N_0 = (0.500)(3.7\times10^{7}\ \mathrm{dis/s})$
$N_0 = 1.68\times10^{16}$ atoms
Mass of strontium

$$= \frac{(1.68\times10^{16}\ \text{atoms})(90.0\ \mathrm{g/mol})}{6.02\times10^{23}\ \text{atoms/mol}} = 2.50\times10^{-6}\ \mathrm{g}$$

$$\text{Specific activity} = \frac{(0.500)(3.7\times10^{7})}{2.50\times10^{-6}} = 7.4\times10^{12}\ \mathrm{dis/s}$$

(b) To determine the activity after 30.0 y:

$$(2.30)\left(\log\frac{N}{N_0}\right) = -\lambda t = -\left(\frac{0.693}{19.9\ y}\right)(30.0\ y) = -1.04$$

$$\frac{N}{N_0} = \frac{A}{A_0} = 0.353 \quad A = 0.353\ A_0 = 0.177\ \mathrm{mCi} = 6.55\times10^{6}\ \mathrm{dis/s}$$

4. Let us first calculate the rate constant and express in $\mathrm{s^{-1}}$.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{(1.28\times10^{9}\ y)(365\,d/y)(24\,h/d)(3.6\times10^{3}\ s/h)}$$

$$= 1.72\times10^{-17}\ \mathrm{s^{-1}}$$

The disintegration rate is an instantaneous rate measured under conditions of essential constancy of the concentration (i.e., the population) of ^{40}K atoms.

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A] = (3.70\times10^{10}\ \mathrm{dis/s\cdot Cu})(10^{-6}\ \mathrm{Ci/\mu Ci})$$

$$= 3.70\times10^{4}\ \mathrm{dis/s\cdot\mu Ci}$$

Since one disintegration measures one atomic event, it is best to express [A] as the number of ^{40}K atoms.

$$[A] = \frac{\text{rate}}{k} = \frac{3.70\times10^{4}\ \text{atoms/s}\cdot\mu\mathrm{Ci}}{1.72\times10^{-17}/\mathrm{s}}$$

$$= 2.15\times10^{21}\ \text{atoms}/\mu\mathrm{Ci}$$

And the corresponding mass is

$$= \frac{(2.15\times10^{21}\ \text{atoms}/\mu\mathrm{Ci})(40\ \mathrm{g}\ ^{40}\mathrm{K/mol})}{6.0\times10^{23}\ \text{atoms/mol}} = 0.143\ \mathrm{g}\ ^{40}\mathrm{K}/\mu\mathrm{Ci}$$

Single Correct Answer Type

5. (c) $^{24}_{11}\mathrm{Na} \rightarrow {}^{24}_{12}\mathrm{Mg} + \underset{(\beta)}{{}^{0}_{-1}\mathrm{e}}$

y = number of half-life $= \frac{60}{15} = 4$

$$N = N_0\left(\frac{1}{2}\right)^{y}$$

$$= 100\left(\frac{1}{2}\right)^{4} - \frac{100}{16} = 6.25\%$$

6. (d) $N_1\lambda_1 = N_2\lambda_2$ at equilibrium

$$\frac{N_1}{t_1} = \frac{N_2}{t_2};\ t_1 \text{ and } t_2 \text{ are half-lives}$$

If $t_1 = t_2$, then $N_1 = N_2$.
If $\lambda_1 = \lambda_2$, then $N_1 = N_2$.
Since, $T_{75} = 2T_{50}$
Hence, if $(T_{75})_1 = (T_{75})_2$
Then $N_1 = N_2$.

7. (b) If T_{75} of $B \rightarrow C$ is 100 min, then $T_{50} = 50$ min.
Thus, $N_\mathrm{A}T_\mathrm{B} = N_\mathrm{B}T_\mathrm{A}$

$$\frac{N_A}{N_B} = \frac{T_A}{T_B} = \frac{100}{50} = 2.$$

8. (b) $\left(1 + \dfrac{N_{\mathrm{U}(238)}}{N_{\mathrm{Pb}(206)}}\right) = (2)^n$

$(1 + 1) = (2)^n$

$\therefore \quad n = 1 = \dfrac{t}{T_{50}}$

$\therefore \quad t + T_{50} = 4.5\times10^{9}$ yr.

9. (b) Based on rock-dating

$$\left(1+\frac{[Pb]}{[U]}=(2)^n\right)$$

$$1+\frac{\dfrac{0.618\times10^{-6}}{206}}{\dfrac{0.238\times10^{-6}}{238}}=(2)^n$$

$$(2)^2=(2)^n$$

$$\Rightarrow \quad n=2$$

$$2=\frac{t}{T_{50}}$$

$$\therefore \quad t=2\times T_{50}=3\times10^9 \text{ yr.}$$

10. (d) $C=Co\left(\frac{1}{2}\right)^y$

$$(3.00\times10^8)=(2.40\times10^9)\left(\frac{1}{2}\right)^y$$

$$\left(\frac{1}{2}\right)^y=\left(\frac{1}{8}\right)=\left(\frac{1}{2}\right)^3$$

$$\therefore \quad y=3 \text{ or } \frac{t}{t_{50}}=3$$

$$\therefore \quad T=3\times t_{50}=36.78 \text{ yr.}$$

11. (d) $N_1=N_0e^{-\lambda_1 t}$ and $N_2=N_0e^{-\lambda_2 t}$

Thus, $\frac{N_1}{N_2}=\frac{e^{-\lambda_1 t}}{e^{-\lambda_2 t}}=e^{-(\lambda_1-\lambda_2)t}=e^{-9\lambda t}$

It is given that $N_1/N_2=e^{-1}$.
Hence, $-9\lambda t=-1\Rightarrow t=1/(9\lambda)$

12. (b) For the half-life $t_{1/2}=28.1y$, the decay constant is $\lambda=\frac{0.693}{t_{1/2}}=\frac{0.693}{28.1y}$

Since the radioactivity decay follows the first order kinetics, we have $\log\frac{[A]}{[A]_0}=-\frac{\lambda}{2.303}t$

Thus, $\log\frac{[A]}{1.0\ \mu g}=-\frac{0.693}{28.1\gamma}\times\frac{20y}{2.303}$

or $\log[A]/\mu g=-0.2142$ or $[A]=0.6107\ \mu g$.

13. (b) $\lambda=\frac{2.303}{t}\log\left(\frac{N_0}{N}\right)$

$$\frac{0.693}{t_{1/2}}=\frac{2.303}{t}\log_{10}\left(\frac{N_0}{N}\right)$$

$$\frac{0.693}{2x}=\frac{2.303}{x}\log_{10}\left(\frac{N_0}{N}\right)$$

$$\frac{1}{2}\log_{10}2=\log\left(\frac{N_0}{N}\right)$$

$$\frac{N}{N_0}=\frac{1}{\sqrt{2}}$$

Fraction undecayed = $\frac{1}{\sqrt{2}}$.

Multiple Correct Answers Type

14. (a)
The radioactive disintegration rate increases considerably with an increase in temperature.

15. (b, d)

Rate $=\frac{0.693}{t_{1/2}}\times$ Number of radioactive nuclei undergoing decay

Rate of decay decreases exponentially with passage of time.

16. (a, b)

$$t_{1/2}=\frac{0.693}{\lambda} \text{ or } \frac{\ln 2}{\lambda} \text{ and } \tau=\frac{1}{\lambda}$$

17. (a, b, c)

$$\lambda=\frac{2.303}{t}\log_{100}\left(\frac{N_0}{N}\right)$$

$$=\frac{2.303}{8}\log\frac{100}{0.39}=0.693=\log_e 2$$

Mean life $\tau=\frac{1}{\lambda}=\frac{1}{\log_e 2}$

$$t_{1/2}=\frac{0.693}{\lambda}=\frac{0.693}{0.693}=1 \text{ hr.}$$

18. (a, b, c, d)

$$N=N_0\left(\frac{1}{2}\right)^n=1\left(\frac{1}{2}\right)^3$$

$=0.125$ mg.
n = Number of half-life = 11.4/3.8 = 3

Activity after 7.6 days = λ × Remaining number of atoms

$$=\frac{0.693}{3.8\times24\times3600}\times\frac{N_0}{4}=5.3\times10^{-7} \text{ dis sec}^{-1}$$

$$\lambda=\frac{0.693}{3.8\times24\times3600}=2.1\times10^{-6}\text{ sec}^{-1}$$

$$\lambda=\frac{2.303}{t}\log\left(\frac{N_0}{N}\right)$$

$$\frac{0.693}{3.8}=\frac{2.303}{5}\log\left(\frac{100}{N}\right)$$

$N=40$ $\quad\therefore$ % decay = 100 − 40 = 60

Matching Column Type

19. (a → p, q, r); (b → p, q, s); (c → p, q); (d → r, s)
The age of the rock has been estimated by uranium dating technique. The uranium ore (rock) which is found in nature is associated with non-radioactive lead which is believed to be the end product of radioactive disintegration of uranium.
By using the half life period of ^{14}C, it is possible to determine the age of various objects.

Integer Type

20. (6) Let N_0 and N be the number of atoms of the radioactive substance present at the start and after 5 minutes respectively.

Rate of disintegration at the start $= \lambda N_0 = 475$ and rate of disintegration after 5 minutes $= \lambda N = 270$

Dividing both, $\frac{\lambda N_0}{\lambda N} = \frac{475}{270} \Rightarrow \frac{N_0}{N} = 1.76$

We know that, $\lambda = \frac{2.303}{t}\log_{10}\left(\frac{N_0}{N}\right)$

$$\lambda = \frac{2.303}{5}\log_{10}1.76 = 0.113 \text{ minute}^{-1}$$

Half life period $= \frac{0.693}{\lambda} = \frac{0.693}{0.113} = 6.1 \approx 6$ minutes.

21. (2) $t_{3/4} = \frac{2.303}{\lambda}\log\frac{1}{1/4}$

$$= \frac{2.303}{\lambda}\log 4 = \frac{2.303}{\lambda}\log 2^2$$

$$= 2 \times \frac{2.303}{\lambda}\log 2 = 2 \times t_{1/2}.$$

Comprehension Type

22. (c) It is a fact.

23. (b)

$$\frac{0.693}{t_{1/2}\,{}^{14}C} = \frac{2.303}{t_{\text{age}}}\log\left(\frac{N_0}{N}\right)$$

$$\frac{0.693}{5760} = \frac{2.303}{11520}\log\left(\frac{N_0}{N}\right)$$

$$\Rightarrow \quad \frac{N}{N_0} = 0.25$$

24. (b) It is a fact.

25. (a)

$$\frac{0.693}{t_{1/2}\,{}^{14}C} = \frac{2.303}{t_{\text{age}}}\log\left(\frac{N_0}{N}\right)$$

$$\frac{0.693}{5760} = \frac{2.303}{t_{\text{age}}}\log\left(\frac{100}{60}\right)$$

$$t_{\text{age}} = 4246 \text{ yrs.}$$

DPP 6.4

Subjective Type

1. In the nuclear reaction ${}^{10}_{4}\text{Be} \rightarrow {}^{10}_{5}\text{B} + {}^{0}_{-1}e$ the basic conversion ${}^{1}_{0}n \rightarrow {}^{1}_{1}p + {}^{0}_{-1}e$

Hence, the precise reaction is

$${}^{10}_{4}\text{Br}(4p, 6n, 4e) \rightarrow {}^{10}_{5}\text{B}(5p, 5n, 4e) + {}^{0}_{-1}e$$

Thus, the mass defect is

$$\Delta m = m_{\text{product}} - m_{\text{reactant}}$$
$$= \{\text{mass of } (5p, 4n, 4e) + \text{mass of an electron}\}$$
$$- \text{mass of } (4p + 6n + 4e)$$
$$= \text{mass of } (5p, 5n, 5e) - \text{mass of } (4p, 6n, 4e)$$
$$= \text{Atomic mass of } ({}^{10}_{5}\text{B} - {}^{10}_{4}\text{Be})$$

Now, in the nuclear reaction ${}^{8}_{5}\text{B} \rightarrow {}^{8}_{4}\text{Be} + {}^{0}_{+1}e$, the basic conversion is ${}^{1}_{1}p \rightarrow {}^{1}_{0}n + {}^{0}_{+1}e$.

Hence, the precise reactions is

$${}^{8}_{5}\text{B}(5p, 3n, 5e) \rightarrow {}^{8}_{4}\text{Be}(4p, 4n, 5e) + {}^{0}_{+1}e$$

Thus, the mass defect is

$$\Delta m = m_{\text{products}} - m_{\text{reactions}}$$
$$= \{\text{mass of } (4p + 4n + 5e) + \text{mass of a positron}\}$$
$$- \text{mass of } (5p + 3n + 5e)$$
$$= \text{mass of } (4p + 4n + 4e) + \text{mass of (electron + positron)}$$
$$- \text{mass of } (5p + 3n + 5e)$$
$$= \text{Atomic mass of } ({}^{8}_{4}\text{Be} - {}^{8}_{5}\text{B}) + \text{mass of 2 electrons.}$$

2. Since $1u = \frac{1}{6.02 \times 10^{23}}\text{g} = \frac{1}{6.02 \times 10^{26}}\text{kg}$

$$E = mc^2 = \left(\frac{1\text{ g}}{6.02 \times 10^{26}}\right)(3 \times 10^8 \text{ m/s})^2$$
$$= 1.49 \times 10^{-10} \text{ J}$$

But

$$1 \text{ MeV} = 10^6 \text{ eV} = (10^6)(1.6 \times 10^{-19} \text{ C})(1.0 \text{ V})$$
$$= 1.6 \times 10^{-13} \text{ J}$$

and so $E = (1.49 \times 10^{-10}\text{ J})\left(\frac{1 \text{ MeV}}{1.6 \times 10^{-13}\text{ J}}\right) = 932 \text{ MeV}$

[A more precise value is 931.5 MeV/u.]

3. One can imagine that everything would seem "natural," with "hydrogen" atoms consisting of one antiproton and one positron, "carbon" atoms having six antiprotons and six neutrons in the nucleus and six positrons outside the nucleus, etc. The "carbon" and "hydrogen" could form "CH_4" by the "usual" rules of covalent bond formation. Nuclear reactions in which electrons were produced would lead to annihilation reactions: $\beta^- + \beta^+ \rightarrow$ energy. Similarly, reaction of material from the two worlds, e.g., ordinary hydrogen and "hydrogen" from the antiworld, would also lead to annihilation reactions : Proton + antiproton → energy.

4. ${}^{235}_{92}\text{U} + {}^{1}_{0}n \rightarrow {}^{139}_{54}\text{Xe} + {}^{94}_{38}\text{Sr} + ?$

The subscripts already balance, so the subscript of the unknown particle(s) must be zero. The superscripts on the right total 3 less than those on the left. There must be three neutrons (${}^{1}_{0}n$) also produced.

$${}^{235}_{92}\text{U} + {}^{1}_{0}n \rightarrow {}^{139}_{54}\text{Xe} + {}^{94}_{38}\text{Sr} + 3{}^{1}_{0}n$$

Note that gamma particles (${}^{0}_{0}\gamma$) might also be produced, but since they are both zero subscript and zero superscript, their presence cannot be deduced by this kind of analysis.

Single Correct Answer Type

5. (b) In a spallation reaction, a high-speed bombarding particle is absorbed by the target nucleus forming a normal nucleus and a large number of light particles.

6. (b) Cadmium rods are used as control rods. These rods absorb neutrons and thereby control the rate of fission.

7. (a) The intermediate nuclei formed is radioactive, i.e., to introduce radioactivity in an element by bombarding with suitable projectile.

8. (c) $\Delta m = m(\text{Th}) + m(\text{He}) - m(\text{U}) = (228.029 + 4.003 - 232.038)\ \text{u}$

$= -0.006\ \text{u}$

Hence $\frac{1}{2}m(\text{He})u^2 = |(\Delta m)|c^2$ or $(u/c) = \sqrt{\frac{21(\Delta m)}{m}}$

or $(u/c) = (2 \times 0.006/4.003)^{1/2} = 0.005.$

9. (d) In reaction

$${}_{21}\text{Sc}^{45} + {}_{0}n^{1} \rightarrow {}_{20}\text{Ca}^{45} + {}_{1}\text{H}^{1}$$

Neutron is attacking while proton is produced along with the product.

10. (c) Molten sodium is used as coolant in nuclear reactors to remove heat generated during the course of nuclear reactions.

11. (b) Liquid alloy of sodium and potassium is used as coolant, it takes away the heat to the exchanger.

Multiple Correct Answers Type

12. (a, d)

In reactions *a* and *d*, charge number is balanced but not mass number.

13. (c, d)

In the nuclear process ${}^{11}_{6}\text{C} \rightarrow {}^{11}_{5}\text{B} + \beta^{+} + \text{X}$, X stands for neutrino.

In the nuclear reaction, ${}^{3}_{1}\text{H} \rightarrow {}^{3}_{2}\text{He} + e^{-} + \text{X}$, X stands for antineutrino.

14. (a, d)

Nuclear fusion is the phenomenon of fusion two or more lighter nuclei to form single heavy nucleus. The rest mass of a stable nucleus is less than the sum of the rest masses of its separated nucleons.

15. (c)

In living material the ratio of ^{14}C to ^{12}C remains relatively constant. When a tissue in an animal or plant dies, ^{14}C decreases because the intake and utilization of ^{14}C do not occurs. A sample of dead tissue is burnt to CO_2 and the CO_2 is analysed for the ratio of ^{14}C to ^{12}C. From this data, the age of the dead tissue can be determined.

16. (a, b)

^{32}P is used for the treatment of leukemia.

Matching Column Type

17. (a → r), (b → s), (c → p), (d → q)

Particle capture reaction: ${}^{238}_{92}\text{U} + {}^{1}_{0}n \rightarrow {}^{239}_{92}\text{U} + \gamma$. The bombarding particle is absorbed with or without the emission of γ-radiations.

Nuclear fission reaction: ${}^{235}_{92}\text{U} + {}^{1}_{0}n \rightarrow {}^{140}_{56}\text{Ba} + {}^{94}_{36}\text{Kr} + 2{}^{1}_{0}n$. In this reaction a heavy nucleus is broken down into two or more medium heavy fragments.

Nuclear fusion reaction: Light nuclei fuse together to reproduce comparatively heavier nuclei. ${}^{3}_{1}\text{H} + {}^{3}_{1}\text{H} \rightarrow {}^{4}_{2}\text{He} + 2{}^{1}_{0}n$.

Spallation reaction: High-speed projectiles with energies approximately 40 MeV may chip fragments from a heavy nucleus, leaving a smaller nucleus. ${}^{63}_{29}\text{Cu} + {}^{4}_{2}\text{He} \rightarrow {}^{137}_{17}\text{Cl} + {}^{16}_{10}n + {}^{14}_{11}\text{H}$

Integer Type

18. (2) ${}_{+1}e^{0} + {}_{-1}e^{0} \rightarrow 2\gamma$ (photons of same energy)

The mass of two electrons is converted into energy.

The energy produced during emission of two photons

$= 2 \times m_e \times c^2$

$= 2 \times 9.108 \times 10^{-31} \times (3.0 \times 10^{8})^2 = 163.9 \times 10^{-15}\ \text{J}$

Energy produced per photon

$$= \frac{16.39 \times 10^{-14}\ \text{J}}{2} = 8.195 \times 10^{-14}\ \text{J}$$

Using Einstein equation,

$E = \frac{hc}{\lambda}$, were c = velocity of light, λ = wavelength of particle

$$\therefore\quad 8.195 \times 10^{-14} = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^{8}}{\lambda}$$

$$\therefore\quad \lambda = \frac{6.625 \times 10^{-34} \times 3.0 \times 10^{8}}{8.195 \times 10^{-14}} = 2.425 \times 10^{-12}\ \text{m}$$

$\lambda = 2.425$ pm.

19. (b) $1\ \text{MW} = 10^{6} \times 24 \times 60 \times 60\ \text{J}$

$$\text{Number of fissions} = \frac{24 \times 6 \times 6 \times 10^{8}}{200 \times 10^{6} \times 1.6 \times 10^{-19}} = 2.7 \times 10^{21}$$

Mass of uranium $= 2.7 \times 10^{21} \times 235 \times 1.66 \times 10^{-24} = 1.05\ \text{g}$

Comprehension Type

20. (c, d)

A moderator slows down neutrons and yield thermal neutrons.

21. (d) Sodium is used as coolant in a nuclear reactor.

22. (b) Only thermal neutrons are produced by moderator.

23. (a, c)

Graphite is a poor conductor of electricity.